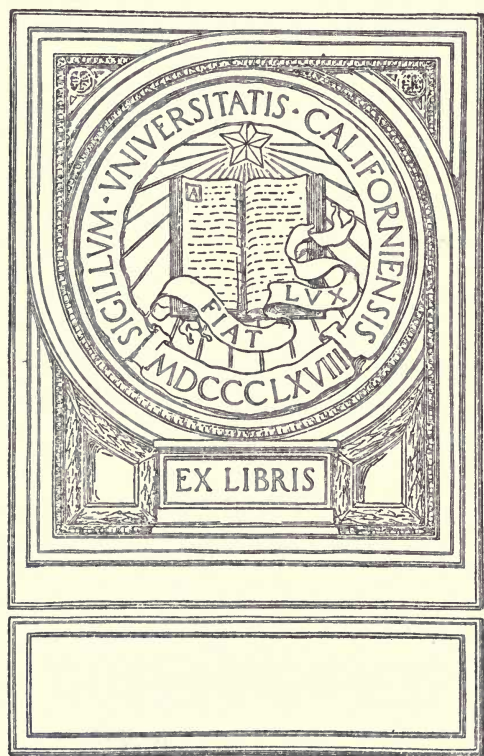


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# Z I R C O N I U M AND ITS C O M P O U N D S

BY  
FRANCIS P. VENABLE



American Chemical Society  
Monograph Series

*BOOK DEPARTMENT*

*The* CHEMICAL CATALOG COMPANY, *Inc.*  
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## GENERAL INTRODUCTION

### American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in

branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's *Handbuch der organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der anorganischen Chemie* and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coordinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of



general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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## PREFACE

I wish to express my obligations in the preparation of this book to the Index to the *Literature of Zirconium* by A. C. Langmuir and Charles Baskerville, and especially to the compendium given by R. Jacoby in Gmelin-Kraut's *Handbuch der anorganischen Chemie*.

I have not sought to record every observation or detail given in the literature, many of which are faulty or erroneous, but only such as seemed to have an essential bearing on the subject. My purpose has been to give a systematic, clear, and sufficiently full account of the chemistry of zirconium which should prove useful in connection with the increasing interest attaching to this element.

This book is affectionately inscribed to my daughter, Louise M. Venable, and to my son, Charles S. Venable, both of whom have rendered invaluable aid in its preparation.

FRANCIS P. VENABLE

*University of North Carolina*  
June, 1921





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# ZIRCONIUM AND ITS COMPOUNDS

## Chapter I

### History

While this element is widely distributed, and fairly abundant, its similarity in general properties to other so-called earths, especially alumina, the difficulty of separation from them, and the absence of any easy characteristic test caused it to escape the notice of the earlier chemists. It is a mark of the careful analytical work done by Klaproth (392) that he should have discovered it and announced its existence conclusively in 1789. In that year he reported that in analyzing the jargon of Ceylon he had obtained 31.5 p.c. silica, 0.5 p. c. iron and nickel oxides, and 68 p.c. of an earth differing essentially from all known to him. This he called Zirkonerde. A few years later Klaproth (393) analyzed also the hyacinth of France and found the same new earth. In 1797 Guyton de Morveau (274) published his analyses of zircons from various localities, confirming the work of Klaproth. About the same time Vauquelin (726) examined this new earth, to which the name zirconia was given, and detailed the preparation and properties of some of its compounds. In 1798 Trommsdorff (711) applied all of the methods then known for the decomposition of this earth but without success, and it was not until 1824 that Berzelius (50) found a method for its decomposition and for the preparation of the element zirconium, though in an impure form. Two years later (53) Berzelius determined its atomic weight.

At various times announcements have been made as to the complexity of zirconium or its being accompanied by some hitherto unknown element. This is not surprising when one considers the large number of other elements which have been recognized as present in zircons, the prolonged operations necessary for complete separations, and the ease with which zirconium forms basic compounds of varying



content and widely differing solubilities. In 1845, Svanberg (692) claimed that in decomposing zircons he had come across another earth which differed from zirconia in the solubility of its chloride, of the double sulphate with potassium and of its oxalate, and which also had a lower atomic weight. This earth he called *noria* and the supposed new element *norium*. In 1853 Sjögren (659) believed that he had found this *noria* in the mineral *catapleiite*. According to his determinations its density was 5.5 while that of zirconia was 4.3. The existence of *noria* was satisfactorily disproved by the works of Berlin (43), Hermann (325), Marignac (468), and Knop (400).

In 1864 Nylander (529) reported the existence of two earths in zirconia, an observation which has not been confirmed. In 1869 Sorby (667) announced that in the Ceylon jargon he had discovered a new element with a peculiar absorption spectrum to which he gave the name *jargonium*, but later (668, 669) found he had fallen into error through the presence of a small amount of uranium, which is commonly present in zircons wherever found. In the same year Church (141) drew the conclusion from his spectroscopic examination that zirconium was accompanied by a new element to which he gave the name *nigrium*. Here again is an illustration of the ease with which a mistake can occur from accompanying impurities, such as thorium, yttria, and the rare earths which are found in the zirconium minerals coming from many different sources.

The announcement by Hofmann and Prandtl (347) that about one-half of the zirconia obtained from *euxenite* from Brevig consisted of a new oxide which they called *euxenerde* and which had a considerably higher atomic weight has not been confirmed by further investigation. Hauser and Wirth (301, 302) working with twelve different minerals secured from widely separated localities failed to get the characteristic reactions reported for *euxenerde*. Furthermore the zirconia was separated by the usual methods and each sample purified by fractionation and the fractions examined spectroscopically with the result that there was no decomposition of the zirconium nor separation of a companion element, only those already known being identified.

### Occurrence

While zirconium can not be ranked among the abundant elements in nature it is widely distributed and found in a number of localities in workable quantities. Since no delicate and characteristic test is

known for it, its presence has failed of detection in many minerals. Traces are easily lost sight of when it accompanies titanium, aluminum, and the rare earths in small amount.

Zirconium is found in crystalline rocks (especially in granular limestone) in chloritic and other schists, in gneiss, syenite, granite, and beds of iron ore. The syenitic rock called "zircon syenite" contains crystals of zircon along with epidote, clæolite, oligoclase, and ægirine. It is found also in pegmatite, sandstone, ferruginous sands, and in a number of minerals in which it is present only in small amounts or traces. So constant is its presence in the older igneous rock that Strutt (688, 689) has made use of its uranium-lead ratio as a means of calculating their relative age. Crystals of zircons are common in auriferous sands and are found in volcanic rocks.

The most widely distributed and abundant mineral containing zirconium is the silicate, known in the common form as zircon. From this the name of the element is derived. It has a hardness of 7.5 and a density varying from about 4.0 to 4.7, averaging about 4.65. As a normal silicate its theoretical composition would be  $\text{ZrO}_2$ , 67.2 p.c.;  $\text{SiO}_2$ , 32.8. The percentage of zirconia varies, however, from 61 to 66.8 p.c. The most common impurity is iron, but quantitative analyses (733) show traces of sodium, potassium, magnesium, calcium, aluminum, iron, lead, tin, uranium, erbium, and other elements, and Linnemann (449) found in addition zinc, copper, bismuth, manganese, cobalt, and nickel. The presence of some of these is doubtless due to infiltrations in the cracks of the crystals from the surrounding soil.

There are references to zircons in very early times. On account of its hardness it was used as a material from which to cut cameos and engraved signets. Intaglii of zircons are not at all uncommon among ancient gems. Under the name of the jacinth it is mentioned by Agricola and Interpe. It is mentioned also in the Book of Revelation. The jacinth seems to have been the colorless or yellowish variety. Brownish, orange, or reddish varieties were known as hyacinths and sometimes confused with topazes and garnets. There would seem to be little reason, however, for the substitution for jacinth in the revised version of Revelation. The Ceylonese called it jargon and the colorless or slightly smoky varieties were sold as inferior diamonds. While resembling the diamond in lustre, they were less brilliant and not so hard and were comparatively worthless. De Lisle in 1783 writes of the Diamant Brut or Jargon de Ceylan. One singu-



lar use is mentioned by Fourcroy, who says, "The hyacinth from Expailly (near Le Puy) in France was formerly placed in collections of the *materia medica* to be used in some pharmaceutic compositions."

The zircons of Ceylon are mainly found in alluvial sands. Those of the Ural Mountains are chiefly in the gold regions. They are also found in Greenland, Norway, Transylvania, Bohemia, the Tyrol, France, Italy, Australia, New Zealand, etc. In the United States the zircon is commonly associated with magnetite sand or ore, and it has been found in a number of states, including North Carolina, South Carolina, Tennessee, Oklahoma, Florida, New York, New Jersey, Pennsylvania, California, Virginia, and others. By microscopic examination of the rocks this list can be greatly extended. Its commercial occurrence is chiefly in masses of pegmatite and pegmatized gneisses, and in these it is often in fairly large crystals, weighing up to fifteen pounds. So far only three localities in the United States are known where it occurs in sufficient quantities for mining. These are on Green River in Henderson County, North Carolina, at Anderson, South Carolina, and near Ashland, Virginia. Shipments have been made from the first-named locality amounting to about 20,000 pounds since 1902 and perhaps 60,000 pounds prior to that date. Very large crystals weighing as much as fifteen pounds have been found at Renfrow, Canada, but the supply seems to be limited. Opaque green zircons have been found in St. Lawrence County, New York, and black ones in New Jersey. Small but very beautiful crystals, some of them deep emerald green, are found near Pike's Peak, Colorado. In the volcanic tufa of Vesuvius it is found in small white and blue octahedra.

The zircons of Ceylon occur mainly in alluvial sands. The amount in the gold regions of the Ural Mountains is said to be large. There appear to be considerable deposits in Greenland and Norway and also in New South Wales.

Microscopic crystals are widely distributed in the sedimentary rocks, the material having been largely derived from the older rocks, e.g., in the variegated sandstones of the Black Forest, in carboniferous limestones, and in the sands of the valley of the Main. Thürach has shown that microscopic zircon is rarely absent from archæan and sedimentary rocks. It also occurs in many igneous rocks and is widely distributed in basalts and dolerites. Its resistance to weathering and attrition causes the zircon to be found in many auriferous, volcanic, and shore sands. The researches of the United States Geo-



logical Survey upon the black sands would tend to show its universal presence in granite and allied rocks.

In color the crystals vary from colorless through a number of colors as amber, smoky, red, reddish-brown, blue, green, black to a dull opaque brown. The small white and blue octahedra of Vesuvius have been mentioned. The finest gem stones come from Ceylon, Mudger, and New South Wales.

Meyer (485) has given the following description of the occurrence and mining of the native zirconia ore in Brazil. The deposits are in the Caldas region which lies partly in the State of Minas Geraes and partly in the State of Sao Paulo, approximately 130 miles north of the city of São Paulo. It is a mountainous plateau, the main elevation of which is about 3600 feet. The surface is undulating, presenting differences in level of from 300 to 600 feet. The whole area is bounded on all sides by ridges rising abruptly from 600 to 1200 feet above the general level and forming a roughly elliptical inclosure with a major axis of approximately 20 miles in length and a minor axis of 15 miles. The predominant rock of the plateau is phonolite.

The ore can be divided roughly into two classes. First, alluvial pebbles ranging in size from one-half inch to three inches in diameter, generally carrying about 90-93 p.c. of zirconia. The pebbles, known as "favas" and having a density of 4.8-5.2, are found along small stream beds and on the talus slopes of low ridges. Second, zirconia ore proper or zirkite, which ranges in shade from a light gray to a blue-black, the lighter colored material carrying a larger percentage of zirconium silicates and showing a minimum content of 73 p.c. zirconia. The blue-black ore generally carries 80-85 p.c. of zirconia.

Prior to the investigations of Derby and Lee (177) this zirkelite was considered identical with baddeleyite. It has now been shown that it is a mechanical mixture of three minerals, namely, brazilite, zircon, and a new and unnamed zirconium silicate carrying about 75 p.c. of zirconia. This new mineral has the same crystal form as zircon but is readily soluble in hydrofluoric acid, while zircon is practically not attacked.

Several large outcrops of the ore occur on the extreme westerly edge of the plateau, one or two boulders weighing as much as 30 tons. Owing to the hardness of the ore it is almost impossible to drill holes for explosives, and in handling large masses it is found necessary to resort to the primitive method of heating the rock and suddenly cooling with water. In some of the deposits the ore occurs in the form

of gravel and large pebbles embedded in a reddish clay. On drying the ore can be separated by screening. It is washed thoroughly clean from ferruginous matter before shipping. Transportation of the ore to the nearest railroad is difficult. From surface indications the deposits are of vast extent. The shipment of this ore reached in 1913 a total of 1,119 tons. The maximum production of ore in the United States (practically all from North Carolina) was reached in 1905 with a yield of 4 tons.

It is evident that the most important commercial source of zirconium is the native zirconia of Brazil whose occurrence has been described. This Brazilian ore is reasonably pure and may be used direct in refractories as zirconia or can be easily converted into the desired compounds, which is much more difficult in the case of zircons. Baddeleyite is the mineralogical name, and distinct fibrous botryoidal, or columnar crystals of this mineral are found in the ore, which is known as brazilite. Jacupirangite is a variety of baddeleyite also crystalline. Besides the occurrence of baddeleyite in Brazil it has been found in the United States, Ceylon, Sweden, and Italy. The commercial ore is often called zirkite and has some zircon mixed with it. Zirkelite is also present and is a variety of zirconium silicate containing about 50 p.c. of zirconia.

Zirconium has been reported (317, 478) as present in certain spring waters and its presence has been detected (615) in the solar spectrum. It has also been reported as having been found in a meteorite, but the identification seems to have been incomplete.

#### LIST OF ZIRCONIUM MINERALS.

Adelfolith or malacone	weathered zircon	p.c.ZrO <sub>2</sub> 47.42
Alvite	weathered zircon	3.9-32.48
Anderbergite	R <sub>3</sub> V <sub>2</sub> Zr <sub>5</sub> (SiO <sub>2</sub> ) <sub>12</sub> ·18 H <sub>2</sub> O	41.2
Arrhenite	hydrated silicotitanate of Zr, Fe, Ce, Er	3.42
Astrophyllite	(SiTiZr) <sub>3</sub> O <sub>16</sub> (MnFe) <sub>4</sub> (KNaH) <sub>4</sub>	4.97
Auerbachite	weathered zircon	55.18
Baddeleyite	native zirconia	up to 99.0
Beccarite	zircon containing Ca and Fe	62.16
Brazilite	see baddeleyite	80.0
Catapleiite	H <sub>2</sub> (Na <sub>2</sub> Ca)ZrSi <sub>2</sub> O <sub>11</sub>	30-40.
Chalkolamprite	a niobate-silicate of Zr	5.7
Cyrtolite	weathered zircon	36-61.
Elpidite	Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> ·Zr(Si <sub>2</sub> O <sub>5</sub> ) <sub>2</sub>	20.5
Erdmannite	basic silicate of cerium earths and ZrO <sub>2</sub>	varying
Eudialyte	Na <sub>13</sub> (CaFe) <sub>6</sub> (SiZr) <sub>20</sub> O <sub>52</sub> Cl	10-20.
Fergusonite	niobate (tantalate) Yt, Ce, U, Th, etc.	up to 7.
Hiortdahlite	zircon pyroxene	21.5
Kochelite	niobate of yttria earths	12.8



## LIST OF ZIRCONIUM MINERALS.

		p.c. $\text{ZrO}_2$
Lovenite	$(\text{SiO}_3)_2 \text{MnCaFe} \cdot (\text{ZrOF})\text{Na}$	30.
Mosandrite	Zr, Th, Ce, Ti silicate	7.4
Oliveiraite	$3\text{ZrO}_2 \cdot 2\text{TiO}_2 \cdot 2\text{H}_2\text{O}$	63.36
Orvillite	$8\text{ZrO}_2 \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$	71.88
Polymignite	metazirconotitanate and tantaloniobate	14-30.
Pyrochlor	niobate-titanate	
Rosenbuschite	zircon pyroxene	20.
Tachyphalinite	weathered zircon	39.
Tantalite	a tantalate (niobate)	up to 11.
Uhlignite	$(\text{ZrTi})\text{O}_5 \cdot \text{Ca} \cdot (\text{TiAl})\text{O}_5\text{Al}$	22.
Wöhlerite	$\text{Si}_{10}\text{Zr}_7\text{Na}_2\text{O}_{42}\text{F}_2 \cdot \text{Ca}_{10}\text{Na}_8$	15-23.
Zirkelite	zirconium silicate	50.

In the following minerals zirconium is found in small amounts: Auerodite, bragite, cerite, columbite, edwardsite, eucrasite, hypserthenite, johnstrupite, leukosphenite, karyocerite, knopite, koppite, mackintoshite, melanocerite, monazite, niobate, nohlite, samarskite, seybertite, sillimanite, sipylite, tritonite, tscheffikinite, tyrite, uhlignite, uraninite, vietingshoffite, xeontime, yttergranate, and zoisite.

The zirconium minerals have been classified under the following types:

1. *Zircon type*. Adelfolith, alvite, anderbergite, arrhenite, auerbachite, benarite, engelhardtite, erdmannite, hiordahlite, ilmenite, malacone, mosandrite, oerstedtite, ostranite, pyrobuschite, tachyaphalinite, zircon.

2. *Acid type*. Astrophyllite— $(\text{SiTiZr})_5\text{O}_{16}(\text{MnFe})_4(\text{KNaH}_4)$ —and elpidite— $\text{Si}_4\text{ZrO}_{10} \cdot \text{Na}_2$ —eudialite, fergusonite, catapleiite, leukosphenite, lovenite, polymignite, wöhlerite.

3. *Oxide type*. Baddeleyite, brazilite, zirkelite.

4. *Tantalate type*. Bragite, chalkolamprite, pyrochlor, tantalite.



## Chapter II

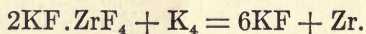
### Zirconium and its Properties

#### Preparation of Zirconium

The preparation of metallic zirconium presents many difficulties and numerous attempts during nearly a century failed to produce the metal reasonably free from impurities. Some of the chief obstacles arise from its strong affinity for oxygen, and hence the difficulty of reducing the oxide and the ease with which the metal is reoxidized at high temperatures; also the readiness with which it absorbs and combines with hydrogen, nitrogen, boron, and silicon, and its tendency to form alloys with the light metals such as aluminum and magnesium.

It was along the line of the reduction of the oxide that the first efforts to produce the metal were made and failed. These were by Trommsdorff (711) in 1798 and Davy (170) in 1808. Attempts at reducing zirconia in a stream of hydrogen failed and it is now known that even had they succeeded the hydride would have been formed if the temperature had not exceeded  $800^{\circ}$ . Nor can the tetrachloride be reduced by hydrogen at a temperature under  $600^{\circ}$ .

In 1824 Berzelius (50) first prepared the metal by the reduction of the double fluoride of zirconium and potassium by means of potassium.



The dried and finely powdered double fluoride was heated in layers of potassium in a small iron cylinder closed at one end, and placed in a platinum crucible, covered with a top. This mixture was stirred with an iron wire and heated over a lamp, first gently and then to low red heat. In this way the reduction went on quietly. On treating the cooled mass with water a little hydrogen was evolved and amorphous zirconium separated. This contained some zirconia. It was further washed with water, digested for six hours at  $40^{\circ}$ – $50^{\circ}$  with equal parts of hydrochloric acid and water, then washed on a

filter with a solution of ammonium chloride, and lastly with alcohol. The product was impure and observations made upon it as to the characteristics of elementary zirconium were consequently inaccurate. Subsequent experiments seem to show that the double fluoride is the best source-material for the preparation of the metal, a tribute to the knowledge and skill of Berzelius, but many modifications in the method as outlined above have been gradually introduced. Franz (230) found the double fluoride  $3\text{KF} \cdot \text{ZrF}_4$ , prepared as minute crystals by precipitation with an excess of potassium fluoride, to be preferable to  $2\text{KF} \cdot \text{ZrF}_4$  but used aluminum as a reducing agent, heating the mixture in a graphite crucible. He obtained an alloy of zirconium, however, containing 1.03 p.c. of aluminum and 0.17 p.c. of silicon. The temperature was kept high to lower the contents of aluminum. Troost (713, 714) repeating the experiment of Berzelius, obtained the same amorphous zirconium mixed with zirconia. His reduction by means of aluminum yielded crystals in the form of oblique prisms which were separated by means of dilute hydrochloric acid and revealed on analysis the presence of both aluminum and silicon. They showed an easy cleavage and had a density of 4.15, were more fusible than silicon, and resisted the action of oxygen at red heat. At white heat a coating of oxide was formed. They combined with chlorine with incandescence and, at fusion temperatures, decomposed caustic alkalis with the evolution of hydrogen. They were slightly soluble in hot sulphuric acid and easily dissolved by aqua regia and hydrofluoric acid.

Wedekind (776) attempted the reduction of the double fluoride with aluminum, obtaining different products according to the method of procedure, which on analysis indicated various alloys with aluminum, namely,  $\text{ZrAl}_2$ ,  $\text{Zr}_3\text{Al}_4$ ,  $\text{ZrAl}_3$ .

He also (785) repeated the method of Berzelius with precautions to prevent oxidation. Sodium was found to be preferable to potassium as the reducing agent. The product was dried at  $200^\circ$  in vacuo, leaving a hygroscopic preparation. This was further heated to  $300^\circ$  in vacuo, becoming then pyrophoric, catching on fire on exposure to air fourteen hours after cooling. The product obtained by Berzelius, he concluded, was a mixture of very finely divided metal and zirconia. Some investigators had suggested that the oxide formed was a sub-oxide. Wedekind's conclusions, however, were against this. The existence of this oxide,  $\text{ZrO}$ , has been maintained by Winkler (817) and Dennis and Spencer (176). The metal in very fine subdivision seems



to be very susceptible to the action of oxygen, nitrogen, etc., probably on account of the large surface exposed.

A zirconium said to be of great purity was prepared by Weiss and Naumann (806). They made use of the Berzelian method, substituting sodium for potassium and further purifying the product. Also commercial zirconium was bought from dealers and purified as follows: The impure metal was pressed into pencils and used as the electrodes in a bomb which had been exhausted of air, then filled with hydrogen and this also pumped out. After several repetitions the hydrogen was reduced to a pressure of 10-11 mm. and the electric current turned on. The zirconium pencils were kept at a distance of 2-3 mm. The current used was one of 60-70 amperes at 20-25 volts. The metal of the positive electrode melted and fell in drops upon the negative electrode which was placed underneath. The metal collected in various experiments was found to range from 99.76 p.c. to 99.89 p.c. pure. When ammonia under diminished pressure was substituted for hydrogen, metal ranging from 99.69 p.c. to 99.81 p.c. pure was obtained, showing that at this temperature zirconium apparently does not react with either hydrogen or nitrogen.

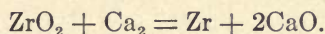
Attempts to reduce zirconia by means of magnesium were made by Phipson (547) and by Bailey (19). The resulting product retained oxide. Also Wedekind (776) prepared amorphous zirconium by heating thin pencils of the double fluoride with magnesium in an electric furnace with a current of 90-100 amperes. This gave a dark, somewhat metallic-like mass containing 94.12 p.c. of zirconium. A later experiment (787) yielded a compact metal with 96.55 p.c. zirconium and 4.14 p.c. oxygen. Warren (761) states that zirconium can be reduced from solutions of its salts by the replacement action of magnesium. Wedekind (777) heating zirconia in a nickel crucible with 40 p.c. over the theoretical quantity of magnesium obtained a colloidal zirconium (purity not determined) which was deep blue in reflected light. On the passage of an electric current the particles migrated with the positive stream, which is opposite to the observation of Whitney (814).

Tucker and Moody (723), who tried the reduction of zirconia by the Goldschmidt method, were unsuccessful. Attempts by Wedekind (773) to reduce zirconia by means of boron yielded the boride. When carbon was used the carbide was formed. Moissan (500) in an electric furnace with a current of 360 amperes and 70 volts brought powdered zircons to fusion and boiling with the giving off



of white fumes. He states that in a carbon crucible he obtained metal containing neither carbon nor nitrogen. On mixing the zircons with an excess of carbon a carbide was formed having 4.22-5.10 p.c. of carbon. This product gradually decomposed in the air. By fusing together the zirconium carbide and zirconium thus prepared he obtained metallic zirconium. The metal was very hard, scratching glass and rubies and having a density of 4.25. The pure metal, however, shows a wide variation from these properties, so Moissan was probably in error as to the purity of his preparatoin.

Wedekind (785) found it possible to reduce zirconia by means of calcium:



Commercial calcium was used (91.8-94.9 p.c. Ca.). The impurities were iron, silicon, and chlorine. The mixture was placed in an iron tube which was then exhausted to 0.5-0.1 mm. pressure. This was heated until the reaction set in and then the reaction moderated by cooling. The porous, baked mass was withdrawn, washed with water, alcohol, dilute hydrochloric acid, and finally acetone, dried, and heated in vacuo. On polishing it gave a fine metallic mirror. Analysis showed 97.7 p.c. zirconium, the remainder being zirconia. It was samples of this preparation which were sent to Burgess and v. Bolton for the determination of the melting point. The density was found to be 6.2. Sander (633) has patented a method for preparing zirconium by heating in vacuo the hydride or nitride under the continuous withdrawal of the gases formed.

Lely and Hamburger (440) have prepared a very pure zirconium by heating zirconium tetrachloride and sodium in a bomb with an electric current. The metal was obtained in laminæ which could be pressed into rods. It was very ductile and gave a mirrorlike surface on burnishing. It was easily oxidized on heating, dissolved in cold hydrofluoric acid, concentrated or dilute, and in concentrated hot sulphuric acid, also in hot aqua regia. The analysis given, namely, 0.2154 grams of metal yielding 0.2915 grams of zirconia, would prove it to be exactly 100 p.c. pure if the atomic weight is taken as 90.6.

Becquerel (35) was the first to attempt the preparation of the metal by electrolysis. Very concentrated solutions of the chloride were subjected to the action of the voltaic pile. The metal was gotten in the form of a black, amorphous powder which was acted upon by air. Troost (714) by the electrolysis of the melted double fluoride

obtained lustrous crystalline laminae which decomposed cold water. Wedekind (774) on repeating this experiment obtained only impure, amorphous zirconium as a gray-black, easily oxidized powder.

*Colloidal zirconium.* Several of the methods for preparing zirconium yield part of it in such finely divided form that it is apparently in the colloidal form. Thus Wedekind (774, 780, 782) reported that when the double potassium and zirconium fluoride is reduced by potassium, the excess of potassium removed by alcohol and the potassium fluoride by washing with water and a solution of potassium nitrate, part of the zirconium in the final washing with water passes through the filter. When this is subjected to dialysis the hydrosol in transmitted light is gray-black in color and in reflected light an opalescent black. It shows a relatively high stability to acid electrolytes while alkaline electrolytes coagulate it. The hydrogel separates in black flocks. Neutral electrolytes cause no direct coagulation. A white precipitate which is redissolved on shaking may be formed. Hydrochloric acid precipitates it on prolonged boiling. Hydrogen dioxide causes immediate precipitation.

Again (777, 814), when zirconia is reduced by an excess of magnesium ground with water, treated with warm, concentrated ammonium chloride solution and then warm, dilute hydrochloric acid part of the solid goes through a filter, giving a colloidal solution which is deep blue in transmitted light. The particles migrate with the positive stream towards the cathode. This latter observation is opposed to that of Whitney (814), who found the supposed colloidal zirconium under the influence of the electric potential to migrate in the direction of the negative stream. This colloidal matter may have been contaminated with the nitride, hydride, or with some partially oxidized metal. A colloidal solution of a similar blue-black color has been prepared from unreduced zirconia.

### Properties of Zirconium

So far as zirconium has been prepared in a condition of reasonable purity it seems to be known only as an amorphous black powder, which when melted is steel-gray and on burnishing gives a lustrous metallic mirror. The existence of a crystalline and a graphitic form has at least not been established. Investigators who have reported them had alloys rather than the pure metal in hand. It is natural that in earlier times their existence should have been surmised from



the analogy of its congener, carbon. The element has been prepared in a colloidal form, though some doubt exists as to its elementary condition in this form. Its degree of hardness has not been satisfactorily determined. The data of Moissan, namely, 4.7, and power to scratch rubies are evidently to be referred to the carbide or mixture of metal and carbide. Marden and Rich (467) gave the hardness as 6.7.

*Specific Gravity.* Many of the determinations of the density are quite unreliable on account of impurities in the samples taken. Such, for instance, are the figures given by Troost (713), 4.15; by Meyer (489), 4.08; by Moissan (500), 4.25. Wedekind (785) out of a series of determinations on metal over 99.5 p.c. pure preferred the figures 6.29. Weiss and Naumann (806), using also very pure metal (99.8 p.c.), reported the density as 6.4. The close accord of the two last observers would lead to the conclusion that 6.4 is to be taken as the density of the pure metal. The atomic volume then is 14.16 (At.wt. 90.6).

*Melting Point.* The discrepancies in the few determinations which have been made of this constant are serious and now that the metal can be prepared in purity a careful redetermination is demanded. Supposedly pure metal was furnished by Wedekind to both v. Bolton and Burgess. The former (89), using a vacuum furnace and Siemens and Halske optical pyrometers, which had a probable error of  $50^{\circ}$  at the temperature used, gave as the results of two experiments  $2330^{\circ}$  and  $2380^{\circ}$  or an approximate mean of  $2350^{\circ}$ . This is near the melting point of zirconia. Burgess (113) used a platinum support so that the possible formation of an alloy was not eliminated. Still the method was tested with iron, chromium, cobalt, nickel, and manganese, where the same possible source of error existed, and results were obtained in accord with the known melting points of these metals. His three experiments with zirconium gave  $1529^{\circ}$ ,  $1533^{\circ}$ ,  $1523^{\circ}$ , and he adopted the figure  $1530^{\circ}$  for the melting point. Marden and Rich (467) gave the melting point as a little over  $1600^{\circ}$ . Guertlar and Pirani (270) give a probable melting point of  $1700^{\circ}$ .

*Specific Heat.* The earliest determination of the specific heat was made by Mixter and Dana (499). The figure obtained was 0.0667 at  $99.7^{\circ}$ . This would give an atomic heat of 6.07. The specimen of zirconium contained silicon and probably other impurities. Wedekind and Lewis (786) found the specific heat to be 0.06725, which would give an atomic heat of 6.1. Later determinations by



Wedekind (785) gave the range for different samples as 0.0656 to 0.0735, or an atomic heat of 6.19 to 6.66. Weiss and Naumann (806) with a very pure specimen obtained the high result of 0.0804, or an atomic heat of 7.31. The latter, if confirmed, would assign to zirconium the highest atomic heat known. All these determinations were apparently made at the range 0°–100°. Dewar (186) has determined the specific heat at temperatures between that of liquid nitrogen and liquid hydrogen, finding it to be 0.0262, which gives an atomic heat of 2.38 at that range.

*Electrical Properties.* Meyer (489), making use of commercial specimens, found zirconium to be diamagnetic and with an atomic magnetism  $k = 0.0114 \times 10^{-6}$  at 17°. Pure amorphous zirconium is a conductor of electricity. When pressed into pencils it can be used as electrodes for the arc. For filaments, rhodium has sometimes been added. Böhm (83) has recorded a number of observations as to the conductivity of zirconium filaments. Owen (533) has examined the thermomagnetic properties of zirconium, determining the specific susceptibility which is equal to the field intensity divided by the density. The determinations were made on "crystallized zirconium."

*Optical Properties.* Karl (382) has reported his experiments upon the triboluminescence of zirconium in compounds. Gladstone (245) found the specific refraction of zirconium to be 0.242 and the atomic refraction 21.9.

*Spectrum.* The earliest examination of the spark spectrum of zirconium was made in 1869 by Thalen (701). This was in the visible spectrum and twenty-six lines are recorded with their intensity on the old scale. They are as follows:

	$\lambda$	$i$		$\lambda$	$i$
Orange	6343.5	3	Indigo	4497.5	4
"	6310.0	3	"	4494.5	4
"	6140.5	1	"	4443.0	4
"	6132.5	3	"	4380.0	4
"	6127.0	1	"	4370.0	4
Yellow	5384.5	4	"	4360.0	4
"	5349.5	3	"	4242.0	4
Green	5190.5	3	"	4241.5	4
"	4815.0	1	Violet	4228.5	4
"	4771.0	1	"	4209.5	4
"	4738.5	1	"	4209.0	4
"	4709.5	1	"	4155.0	2
"	4686.5	1	"	4149.0	2

The spectrum of zirconium is especially rich in ultra-violet lines. Exner and Haschek (214) have measured 1424 of these lines. The

zirconium used was prepared by the Moissan method and hence probably contained carbon and other impurities. The chief lines and their intensity (Rowland's scale) are given by Gmelin and Kraut.<sup>1</sup>

$\lambda$	$i$	$\lambda$	$i$
3392.20	20	3958.39	20
3438.39	20	3991.31	20
3496.40	20	3999.18	20
3556.89	20	4149.43	20
3698.41	20	4209.21	20
3751.85	20	4380.12	20
3836.98	20		

The arc spectrum, according to Rowland and Harrison (616), gives 820 lines, of which the chief are the following:

$\lambda$	$i$	$\lambda$	$i$
3392.14	10	4227.94	10
3496.38	10	4239.49	10
3890.49	10	4282.36	10
3891.53	10	4507.32	10
3929.71	10	4535.90	10
3973.63	10	4575.69	10
4081.40	10	4688.00	10

Vehle (731) has measured the arc spectrum in terms of the international normal. As a means of spectroscopic detection de Gramont (253) has recommended the use of the five lines in the blue between 481.6 and 469, especially 474.0.

The measurement of the ultimate rays of greatest photographic sensibility (international normal) has also been given by de Gramont (254) as follows:

<i>Rays</i>	1/100	1/1000	5/10000	1/10000	5/100,000
3698.16	+	?	.	.	.
3572.47	+	+	?	.	.
3505.66	+	+	+	.	.
3496.20	+	+	+	+	.
3438.23	+	+	+	?	.
3391.98	+	+	+	+	+
3273.04	+	+	.	.	.

The decomposition of the zirconium lines into their components has been investigated by Moore (503). The visible arc spectrum has also been mapped by Eder and Valenta (206). They found it easiest to obtain by using the halides, as the oxy-compound gave a continuous spectrum from the glowing oxide. In the oxy-hydrogen flame the spectrum was also continuous. Eder (205) has also measured the

<sup>1</sup> Gmelin and Kraut. Handbuch der anorg. Chem. Bd. VI, p. 7.



lines in the red and infra-red. Du Bois (86) has studied the selective absorption and the Zeeman effect. Moseley (506) has recorded the high-frequency spectrum.

*Chemical Conduct.* 1. *Towards other elements.* According to Wedekind (785), amorphous zirconium when heated below  $700^{\circ}$  absorbs hydrogen, combining with it to form a solid hydride which is fully dissociated at  $800^{\circ}$ . It combines readily with oxygen, burning with brilliant light when heated considerably below red heat. The denser and much purer metal, however, was only slowly oxidized (789) when heated in air up to  $270^{\circ}$ . Towards nitrogen amorphous zirconium shows a like readiness of combination, forming a nitride. The formation of this nitride is reported by several investigators when, in preparing the metal, the product was heated in the presence of air. At high temperatures ( $700^{\circ}$ – $1000^{\circ}$ ) zirconium does not combine with hydrogen or nitrogen, the temperature being above that for dissociation of the compounds. The oxide is stable at very high temperatures. When the metal is heated with carbon a carbide is formed, which if rich in carbon is gradually decomposed in air but otherwise seems stable. Zirconium readily combines at high temperatures with silicon and boron. With copper, silver, aluminum, and metals of the iron group and some other metals alloys are formed, but not with lead or tin (467). Chlorine and bromine act upon zirconium when heated, forming the tetrahalides. Ammonia passed over heated zirconium gives the nitride. Sulphur also combines with the metal when heated. Red phosphorus gives a black powder.

2. *Behavior towards hydroxides and oxides.* When heated with alkali hydroxides hydrogen is evolved, according to Troost (714), but this action takes place only so long as water is present. However, Wedekind reports solutions of alkali hydroxides to be without action (789). This discrepancy is doubtless due to the fact that Troost did not have as pure a metal. Fused with alkali hydroxides the action is only partial, with potassium nitrate it is explosive, and with copper oxide or lead oxide it is very energetic. Other oxides, as chromic, show no action up to  $800^{\circ}$  (789). Silica is reduced at a bright red heat (776). Boron trioxide and titanous oxide are also reduced. The great affinity of zirconium for oxygen has suggested its use as a reducing agent and the use of its alloys as cleansing agents in metallurgical operations.

*Action of Acids.* Hydrofluoric acid easily dissolves the metal in the cold, even the dilute acid acting upon it. Concentrated hydro-



chloric acid acts very slightly and nitric acid not at all. Hot concentrated sulphuric acid acts energetically, giving off sulphur dioxide (789). Aqua regia also reacts readily.

*Position in the Periodic System.* The position of zirconium in the periodic system was first settled by its analogies with the elements of the fourth group. In the first place, there is the formation of the typical oxide,  $\text{ZrO}_2$ , and the occurrence of this free and combined with  $\text{SiO}_2$ . Then there is the formation of the tetrahalides and the ready hydrolysis of the tetrachloride. From vapor density determinations of the tetrachloride, Deville and Troost (185) have shown the formula to be  $\text{ZrCl}_4$  and hence the valence of zirconium four. Also the molecular weight determination of the acetylacetonate (69) gives the formula  $\text{ZrR}_4$ . Furthermore, there is the amphoteric reaction of the hydroxide and the formation of zirconic acid,  $\text{H}_2\text{ZrO}_3$ , which is comparable with  $\text{H}_4\text{CO}_3$ ,  $\text{H}_2\text{SiO}_3$ ,  $\text{H}_2\text{TiO}_3$ , and  $\text{H}_2\text{SnO}_3$ . These five elements were grouped together by Mendeleeff in his first table arranged according to the atomic weights. By means of the high-frequency spectrum Moseley (506) and Friman (235) have determined the atomic number as 40, which confirms the above arrangement and settles the position of the element.

*Atomic Weight.* Determinations of this constant for zirconium have been made by Berzelius (53), Hermann (319), Marignac (468), Weibull (794), Bailey (22), Venable (736), Venable and Bell (744). A resumé of these is given in the following table:

<i>Date</i>	<i>Author</i>	<i>Ratio</i>	<i>No. Analyses</i>	<i>Atomic Weight</i>
1. 1826	Berzelius	$\text{Zr}(\text{SO}_4)_2:\text{ZrO}_2$	6	89.46
2. 1881	Weibull	" "	7	89.54
3. 1889	Bailey	" "	8	90.63
4. 1881	Weibull	$\text{Zr}(\text{SeO}_4)_2:\text{ZrO}_2$	5	90.79
5. 1860	Marignac	$\text{K}_2\text{ZrF}_6:\text{K}_2\text{SO}_4$	4	90.03
6. 1860	Marignac	$\text{K}_2\text{ZrF}_6:\text{ZrO}_2$	4	91.54
7. 1898	Venable	$\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}:\text{ZrO}_2$	10	90.81
8. 1844	Hermann	$\text{ZrCl}_4:?$	1	88.64
9. 1844	Hermann	$2\text{ZrOCl}_2:9\text{H}_2\text{O} \cdot \text{ZrO}_2$	2	89.98
10. 1917	Venable and Bell	$\text{ZrCl}_4:4\text{Ag}$	13	91.76

It is evident that the present uncertainty as to this fundamental constant leaves it in an unsatisfactory condition and more accurate determinations are necessary. The figure recommended by the International committee on Atomic Weights, which does not consider series 10, is 90.6.

### Salts of Zirconium

These fall into three classes. 1. Normal zirconium salts in which zirconium is the metallic cation with a valence of four. This is seen in the halides  $\text{ZrF}_4$  and  $\text{ZrCl}_4$ , also in combination with strong acids,  $\text{Zr}(\text{SO}_4)_2$  and  $\text{Zr}(\text{NO}_3)_4$ . In the preparation of these water must be rigidly excluded on account of the ease of hydrolysis. The number of these definitely known, outside of the binary compounds, is small and the existence of some reported is open to question.

2. Zirconyl and basic zirconyl salts where the cation is the radical  $\text{ZrO}$  (118). These are the product of the hydrolysis of the normal salts and form the much larger number of the known compounds of this element. The tendency often is for more than one zirconyl radical to enter into the combination. In some cases the increasing basicity seems to have no definite stopping point, as is indicated by the continuous dissolving of the hydroxide in solutions of the sulphate or nitrate until a thick, gumlike product is obtained on reaching the limit of solubility. In the case of organic acids there are often formed basic salts whose composition depends upon the concentration, the temperature, and the relative proportions of the constituents added.

In the preparation of certain compounds by precipitation methods it has been found that the precipitate forms sometimes only after a considerable lapse of time or upon heating the solution. This is especially the case where weak acids, such as the organic acids, are concerned. The compounds thus formed are found to be more or less highly basic zirconyl salts or mixtures of such. It seems reasonable to infer that the acid radical of the precipitant used forms only soluble compounds with the less hydrolyzed salts and insoluble ones with the more basic. It is possible also that in some cases these are not true chemical compounds but adsorption compounds in which the acid radical has been adsorbed by the colloidal hydroxide. Some of these products are distinctly gelatinous and can be washed and filtered with difficulty. On the other hand, some are granular and some distinctly crystalline. The hypothesis of colloidal compounds is especially probable wherever the acid radical can be practically removed or greatly reduced in amount by repeated washings of the precipitate, as is true with iodic acid and some organic acids. When, however, analysis reveals the same basic compound as being formed under varied conditions of dilution, etc., as is the case with the basic chro-



mate, it may be fairly assumed that a definite chemical compound has been formed.

There has been little system in the assignment of formulas to the basic zirconyl compounds. Some have written them simply in the ratio of the zirconia to the acid anhydride, as  $2\text{ZrO}_2 \cdot \text{SO}_3$ . Others report this basic zirconyl sulphate as  $\text{ZrO}_2 \cdot \text{ZrOSO}_4$ . Perhaps the most common formula is  $\text{Zr}_2\text{O}_3\text{SO}_4$ . Such formulas fail to make clear the known facts. These substances are often gelatinous and, when hydrolysis is far advanced, the solutions become opalescent. On dialyzing the solutions leave zirconyl hydroxide as a hydrogel. Even the crystalline basic salts dialyze with difficulty and show partly colloidal properties. They have been called half-colloids. Electrolytic dissociation shows often a migration of the zirconyl radical as an anion or a distribution of the zirconium between the anions and cations. It is well known that the migration of a colloid is largely influenced by the medium. Furthermore, there is practically always water of hydration or crystallization present. Considering these facts, it is suggested that the most suitable formula for these basic salts would have to include the zirconyl hydroxide. Thus  $\text{ZrO}_2 \cdot \text{ZrO} \cdot \text{SO}_4$  becomes  $\text{ZrO}(\text{OH})_2 \cdot \text{ZrOSO}_4$  and  $\text{Zr}_2\text{O}_3\text{Cl}_2$  becomes  $\text{ZrO}(\text{OH})_2 \cdot \text{ZrOCl}_2$ . This reveals at a glance the stepwise formation of the colloid and the liberation of the acid, e.g.,  $\text{ZrCl}_4 + \text{H}_2\text{O} \longrightarrow \text{ZrOCl}_2 + 2\text{HCl}$ ;  $2\text{ZrOCl}_2 + 2\text{H}_2\text{O} \longrightarrow \text{ZrO}(\text{OH})_2 \cdot \text{ZrOCl}_2 + 2\text{HCl}$ . Where several molecules of  $\text{ZrOCl}_2$  are hydrolyzed at one step more complex products will result. This method of writing the formulas has therefore been adopted throughout this text wherever accurate knowledge of the composition of the substance was available.

3. Zirconates. Zirconyl hydroxide  $\text{ZrO}(\text{OH})_2$ , which may be written  $\text{H}_2\text{ZrO}_3$ , here functions as an acid and is called zirconic acid. It combines with strong bases, giving zirconates as  $\text{Na}_2\text{ZrO}_3$ ,  $\text{CaZrO}_3$ , etc.

### Valence

While zirconium is quadrivalent in all of its well-recognized compounds, a possible hydride has been reported (67) which may have the composition  $\text{ZrH}_2$ . The existence of a monoxide  $\text{ZrO}$ , which would also be bivalent, has been maintained by some investigators, but the evidence for it is not satisfactory.



## Chapter III

### Compounds of Zirconium with the Elements

#### Zirconium and Hydrogen

*Zirconium Hydride.* The formation of a gaseous zirconium hydride with a supposed composition corresponding to the formula  $\text{ZrH}_4$  has been reported but on insufficient evidence and without analytical data. Later work seems to disprove the existence of such a compound.

Winkler (817, 818) prepared a hydride during the reduction of zirconia by magnesium in a stream of hydrogen. The product was cooled under hydrogen and heated again in an atmosphere of hydrogen. On treating with dilute hydrochloric acid abundant hydrogen was obtained by the action of the acid on unchanged magnesium. A peculiar, disagreeable odor was noted. The gas also gave with silver nitrate solution a dark precipitate in which no zirconium was detected. The product left after freeing from magnesium was a black powder, unattacked by ordinary reagents, easily filtered, but giving a colloidal solution on washing. It was readily oxidized after drying. Analyses of several samples showed it to be a mixture of zirconia and the metal or hydride with an average of 0.73 p.c. of hydrogen. Matignon (469) observed the absorption of hydrogen by zirconium when heated and concluded that a hydride had been formed.

Wedekind (773) noticed that a gas was liberated when the product obtained by reducing zirconia with boron was treated with dilute hydrochloric acid. It had an unpleasant smell, blackened paper moistened with silver nitrite and burned with an almost colorless flame. He came to the conclusion that the gas was hydrogen mixed with a small amount of boron hydride.

Wedekind (785) also analyzed a commercial product which was claimed to be  $\text{ZrH}_4$ . It was a soft, grayish-black powder, burning with the formation of water and yielding analytical results which agreed with the formula  $\text{ZrH}_2$ . He also prepared this hydride by heating metallic zirconium in a Heraeus furnace filled with hydrogen

under a pressure of one-half atmosphere. The temperature was carried up to  $700^{\circ}$  and then slowly lowered. The hydrogen may be entirely driven off above  $800^{\circ}$ . The dissociation temperature, therefore, lies between  $700^{\circ}$  and  $800^{\circ}$ . The evidence seems to be against this being merely absorbed hydrogen and such as to admit of the conclusion that zirconium forms a definite hydride in which it is bivalent. This would correspond with the known hydrides in the fourth group,  $TiH_2$ ,  $LaH_2$ , and  $ThH_2$ , though some of these may also require further proof of their existence, but the existence of such a compound lacks confirmation.

### Zirconium and Oxygen

*Zirconium Oxide.* The only definitely known oxide of zirconium is the dioxide or zirconia,  $ZrO_2$ , corresponding to  $CO_2$ ,  $SiO_2$ ,  $TiO_2$ , and the oxides formed by the other members of the fourth group. There is no satisfactory evidence of the existence of a suboxide,  $ZrO$ . Certainly no such oxide has been prepared or separated, though several investigators have inferred its existence in order to explain observations made by them. For instance, the readiness with which the metal, as prepared by the magnesium reduction, oxidizes when exposed to the air has been assumed as due to the presence of this monoxide, but a pyrophoric condition is not unusual with metals in a state of fine subdivision. Also the increase in weight when oxidized has been taken as a measure of the total oxygen present in combination and from this a formula  $ZrO$  calculated (767) whereas the original product of the reduction in preparing the metal was most probably a mixture in unknown proportions of zirconium, zirconia, and zirconium hydroxide, and hence the data were insufficient for calculation. Schwarz and Deisler (653) have shown that a monoxide is not formed by the reduction of zirconia by magnesium but a mixture of zirconia and the metal together with a small amount of magnesium zirconide. The migration of the so-called colloidal zirconium, as observed by Whitney and Oder (815) in the direction of the negative stream has been cited as a further argument for the existence of  $ZrO$ , but this is at variance with the observations of Wedekind (777). Besides, the exact nature of this colloidal zirconium seems to vary somewhat according to the method of preparation and there are indications that at times zirconia is present, or rather the colloidal hydroxide. Wedekind (780) seems to have failed to obtain  $ZrOCl_2$  by the chlorination of the colloidal solution prepared by the Berzelius



method, which would be expected to form if  $\text{ZrO}$  were present. The oxide,  $\text{ZrO}$ , therefore, is not known to exist separately but, as will be seen later, the radical zirconyl is found in a large number of compounds.

*Zirconium Dioxide.* This oxide,  $\text{ZrO}_2$ , known as zirconia, occurs uncombined in small amounts in Ceylon and other localities, and in commercial quantities in Brazil at Jacupiranga, in the State of São Paulo, and also in the State of Minas Geraes. It is known mineralogically as baddeleyite, and that which comes from Brazil as brazilite. The ore is found in alluvial pebbles from one-half to three inches in diameter, containing from 90 to 93 p.c. of zirconia. It is found also in a form in which there is a larger percentage of zircon and another silicate differing from zircon by its solubility in hydrofluoric acid. This ore, a mixture of brazilite, zircon, and zirkelite, is known as zirkite and carries from 80 to 85 p.c. of zirconia. This native zirconia contains helium and argon besides carbon dioxide, nitrogen, oxygen, and hydrogen. The abundance and lesser cost of this zirkite make it the chief commercial source of zirconia and the other compounds. Apart from this native zirconia the only other practical source of zirconia is the zircon, at present mined only in the United States in the mountain regions of North Carolina. This is found chiefly in Henderson County in a pegmatitic dyke which is about 100 feet wide. The upper portions of the dyke are much decomposed and kaolinized to a depth of 40 feet or more. The zircons are well crystallized, easily separated by hand and washed free from soil. There is no systematic mining carried on and only a few tons have been shipped out.

*Purification of native zirconia.* For many purposes native zirconia can be used without further treatment. Such uses, for instance, are as a refractory and for furnace linings. However, for the preparation of enamels, salts, and for other uses requiring purity of materials the impurities must be separated. By fusion with an alkali hydrogen sulphate and leaching with water acidulated with sulphuric acid a solution of the sulphate is obtained. Much of the iron present may be removed by using a small amount of water for the first washing and rejecting this. The solution of the sulphate yields the hydroxide on the addition of ammonia solution. This is dissolved in dilute hydrochloric acid and the zirconyl chloride purified by recrystallization from concentrated hydrochloric acid. On ignition of the chloride



zirconia is left, but small amounts of chlorine are persistently retained.

A more economical method has been patented for large-scale production (330). The ore is heated with excess of lime and an amount of carbon insufficient for the reduction of the lime. Calcium carbide may be used in the place of the carbon. The product is treated with hydrochloric acid, the silica removed, and the zirconyl chloride then purified. Other methods of preparation are referred to under Patents. (See 12, 29, 250, 310, 330, 380, 444, 454.)

*Preparation of zirconia from zircons.* The most direct method is by subjecting powdered zircons to the high temperature of the electric furnace. The silica and oxides of iron and certain other metals are volatilized and the zirconia is left in quite a pure condition. This method was first suggested by Troost (715). There is loss of zirconia by volatilization at a very high temperature.

Finely powdered zircon can be brought into solution by fusion. A number of different fluxes have been utilized. Marignac (468) prepared the fluoride by fusing powdered zircon with an excess of potassium hydrogen fluoride. The melted mass was allowed to cool, powdered, boiled with water to which some hydrofluoric acid had been added, and the potassium fluozirconate crystallized out. On the addition of sulphuric acid, evaporating to dryness, and igniting strongly there was obtained a mixture of zirconia and potassium sulphate from which the latter could be removed by leaching with water. Or, as recommended by Hornberger (324), the evaporation can be carried to a point at which all of the hydrofluoric acid and most of the sulphuric acid have been driven off, then dissolved in water, and precipitated by ammonium hydroxide.

A more satisfactory method (733) is to fuse in a nickel crucible 400 grams of NaOH, 20 grams of  $\text{Na}_2\text{F}_2$ , and 100 grams of powdered zircon which will pass through a 100-mesh screen. The heat of an ordinary burner is sufficient and the decomposition takes place in from ten to fifteen minutes. The sodium fluoride should of course be well dried. The sodium hydroxide is first melted and the fluoride then added. After bringing the melted mass to a fairly high temperature the zircon is gradually added. Rapid evolution of gas follows the introduction of the powder, the mass being kept well stirred by a nickel stirrer. Much seems to depend upon the reaction being carried through rapidly at a high temperature. The amount of un-attacked zircon should not exceed 0.5 p.c. The melted mass is poured

out upon pieces of sheet nickel. While still hot it is broken off and plunged into hot water. The sodium zirconate is left undissolved, though a negligible portion will go into solution. This zirconate is then dissolved in dilute hydrochloric acid and evaporated to dryness, this being repeated to separate any silica and to drive off such hydrofluoric acid as remained. The dried mass is leached with dilute hydrochloric acid and zirconium precipitated as hydroxide with ammonia. This hydroxide is dissolved in hot concentrated hydrochloric acid, the solution evaporated to dryness and the crude zirconyl chloride washed with ether, thus removing most of the iron present. The iron can be reduced to a trace by the phosgene method (762). The zirconyl chloride is then repeatedly crystallized from boiling hydrochloric acid. This chloride still retains some silica which may be removed by dissolving in water and filtering. Several crystallizations from water give a very pure chloride. For the complete removal of all impurities it is necessary to transform this oxychloride into the tetrachloride and sublime it repeatedly. On ignition the chloride yields the oxide, which retains some chlorine even after prolonged heating at 700°–800°. For the pure oxide it is necessary to precipitate the hydroxide, wash, and ignite.

Fusions of zircon have been made with the caustic alkalies alone (45, 202, 480); also alkali carbonates (45, 808); also potassium hydrogen sulphate. Stolba (683) decomposed zircon by heating with a solution of sodium hydroxide under pressure. By heating zircon in the electric furnace with carbon, or better, lime and carbon, the carbide is formed. This can be dissolved in aqua regia and zirconium hydroxide precipitated by means of ammonium hydroxide (585, 792). The yield is reported as only fair.

Crystallized zirconia can be prepared by the action of boric acid upon zirconium tetrafluoride heated in a carbon crucible. The reaction is  $3\text{ZrF}_4 + 2\text{B}_2\text{O}_3 = 3\text{ZrO}_2 + 4\text{BF}_3$ . The boron fluoride is volatilized and the zirconia is left in the form of dendritic crystals resembling those of ammonium chloride (184). It has also been prepared quite pure as white tetragonal crystals by dissolving zirconia in melted magnesium chloride. The crystals separated out on cooling (346) as white tetragonal prisms and had a density of 5.74. Moissan (500) obtained a vitreous crystalline mass showing dendritic form on fracture by bringing zirconia to full boiling in an electric furnace by means of a current of 360 amperes and 70 volts. Abundant vapors of zirconia also came off. The form of zirconia crystals has also



been reported (586) as quadratic and hexagonal. Berzelius reports zirconia as dimorphous. It has been reported as isomorphic with silica. Native zirconia, baddeleyite, is monoclinic, often twinned, and with perfect cleavage. It has a negative double refraction, a density of 5.41, and hardness of 6 to 7 (360, 361).

*Properties.* The heat of formation of zirconia by direct oxidation of the metal is:  $\text{Zr} + \text{O}_2 = \text{ZrO}_2 + 1958.7 \text{ cal.}$  (498). It forms a white, impalpable powder which is easily swept away in the process of ignition; also a rough, coarse powder which is hard to crush completely and scratches glass. If prepared by the gradual dehydration of the hydroxide and then raising the temperature to  $800^\circ\text{--}1000^\circ$  it forms a compact, semi-vitrified mass. The density has been variously reported as 5.45, Hermann; 5.50, Sjögren; 5.49, Venable and Belden; 5.85, Nilson and Petterson; 5.66, Ruer; 5.89, Bradford. The melting point has been given as  $2563^\circ$  at 30 mm. pressure (626),  $2700^\circ$  (762), and  $2950^\circ$  (97), and is next to the highest melting point for any metallic oxide. The melting point of  $\text{MgO}$  is  $2800^\circ$ . The specific heat is 0.1076 (533) and it is diamagnetic (5). It melts and is volatilized in an electric furnace, and the melting point and beginning of vaporization are said to lie quite close together. The boiling and vaporization can be readily observed. This boiling point has been fixed by Mott (509) at  $4300^\circ$ . The coefficient of expansion is low, namely, 0.00000084, about the same order as that of silica. The conductivity for heat and electricity is also low. The porosity is low (under 1 p.c.) and vessels made of it are impervious to most liquids. When heated in the oxy-hydrogen flame it gives off a very brilliant light with comparatively little heat and yields a continuous spectrum. Coblenz (147) has investigated the diffuse reflecting power of zirconia.

*Chemical Conduct.* Early attempts to reduce zirconia failed (170, 711). It is partially reduced on ignition in a reducing flame (29). Dissociation begins at about  $2500^\circ$ . Ordinary reducing agents, such as hydrogen, do not have any action upon it. Its reduction in the electric furnace by means of carbon begins at  $1400^\circ$ , a carbide being formed (257). Boron and silicon also reduce it, forming respectively a boride and silicide (723, 791). Various metals, such as aluminium and magnesium, also reduce zirconia, partly alloying with the metal. Various agents, such as carbon tetrachloride and carbonyl chloride, bring about double decomposition, forming the tetrachloride and carbon dioxide.

When mixed with carbon and heated zirconia is acted upon by

chlorine and bromine with the formation of the tetrachloride and tetrabromide. It is also acted upon by phosphorus pentachloride when heated in a closed tube. When a mixture of chlorine and carbon tetrachloride is passed over zirconia heated to  $300^{\circ}$ – $400^{\circ}$  zirconium tetrachloride is formed.

When zirconia is ignited it becomes practically insoluble in all acids except hydrofluoric. The discrepancies in the statements as to its solubility in other acids seem to be due to differences in the degree of ignition.

Zirconia is readily dissolved in melted caustic alkalis with the formation of zirconates. When added to melted alkali carbonates carbon dioxide is evolved, but the formation of zirconates is more difficult and only partial. Melting with certain chlorides also yields zirconates. When melted with the bisulphates soluble salts or double salts are obtained. Those with potassium are more difficultly soluble. It is not dissolved in melted boric acid (747).

### Zirconium and Hydrogen and Oxygen

*Zirconium Hydroxide.* This is usually prepared by precipitation from a solution of a zirconyl salt. When an alkali hydroxide is used it is almost impossible to wash the precipitate entirely free from the alkali. Even when ammonia is used prolonged washing is necessary in order to secure the pure hydroxide. The precipitated hydroxide is bulky and gelatinous, resembling aluminum hydroxide. On drying it forms a semi-opaque, vitreous mass, cracking and breaking up on shrinking. After draining on the filter it retains as much as 95 p.c. of water; air-dried, the water content is 47 p.c. (42); dried in vacuo, there is still left about 20 p.c. of water (171, 536). After several weeks' standing over sulphuric acid the weight becomes nearly constant. The water content was found to be 22.89 and 23.01 p.c. (326, 466). In these experiments the precipitation and washing took place in the cold and evidently normal hydroxide was obtained when dried over sulphuric acid. The calculated percentage of water for  $\text{Zr}(\text{OH})_4$  is 22.69. By washing the fresh precipitate once with alcohol and then ether the percentage of water was reduced to 26.50; washing with petroleum ether the water was reduced to 26.44, a mean of several experiments (743).

Dried at  $100^{\circ}$ , whether precipitated hot or cold, the compound  $\text{ZrO}(\text{OH})_2$  is left (50, 537, 466). This partial dehydration takes



place in the hot precipitation when the solution is heated to 85° or over (42), the precipitate being dried at 100° (50) or 140° or higher (42), representing then a fairly stable compound. This is the zirconyl hydrate. Van Bemmelen reports that there is no further loss of water up to 200°. At 300° something over one-half p.c. of water is left and the last traces of water can be removed only by heating to a much higher temperature. The addition of water does not restore water of hydration to the once partially dehydrated hydroxide.

The earlier observation (171) that after all water had been removed and the oxide was further heated there was a sudden loss of potential energy with emission of light has been partially confirmed and the conditions more accurately fixed, it having been reported that sometimes the phenomenon failed to appear (42, 600). The light appears at about 300°, but only when the hydroxide has been partially dehydrated at a somewhat lower temperature, retaining a small fraction of the water (less than 1.9 p.c.). The heat of this change,  $\text{ZrO}(\text{OH})_2 = \text{ZrO}_2 + \text{H}_2\text{O}$ , is about 9.2 cal. to the gram of zirconia. When heated higher there are sudden small explosions with the production of extremely fine powder (619). This doubtless partly accounts for the loss of zirconia in quantitative determinations even under all the usual precautionary conditions.

The normal  $\text{Zr}(\text{OH})_4$ , or cold precipitated hydroxide, is practically insoluble in water. It is readily dissolved by concentrated or dilute inorganic acids to form salts though only sparingly soluble in hydriodic. Among the organic acids oxalic is the most reactive, dissolving it nearly as rapidly as some of the inorganic acids. Saturated solutions of tartaric and citric acids and glacial acetic acid dissolve very little (743).

Zirconyl hydroxide,  $\text{ZrO}(\text{OH})_2$ , which is precipitated from hot solutions, is more slowly soluble in dilute inorganic acids, dilute hydrochloric or dilute nitric acid dissolving only about 1:100, and dilute oxalic acid about half as much. If, however, the precipitate stands for some days in contact with the acid it is dissolved to about the same extent as when precipitated cold (743). The chief difference noted in the case of concentrated acids is that some act more slowly.

Ammonia (Sp. Gr. 0.9) does not seem to dissolve the hydroxide appreciably. When diluted it dissolves about 1:10,000. Potassium or sodium hydroxide have a decidedly greater solvent action, especially the latter. Presumably a compound is first formed which is then dissolved. If a concentrated solution of an alkali hydroxide

saturated with zirconium hydroxide is diluted a portion of the hydroxide will be precipitated, probably as zirconate (747). Certain salts of ammonia exert a greater solvent action than the hydroxide. A saturated solution of the commercial carbonate dissolves about 1:100 and an ammoniacal solution of ammonium tartrate has a somewhat lesser action. The density of the hydroxide precipitated cold and containing 25.97 p.c. of water is 3.25 (743).

*Colloidal Zirconium Hydroxide.* This colloid has been prepared by the dialysis of a zirconyl nitrate solution. The liquid appears clear in transmitted light but cloudy in reflected and contains 1.98 grams of zirconia to the 100 c.c. It is stable when boiled and fairly stable towards electrolytes. The hydrosol is positively charged (67, 68). Also by the dialysis of a zirconyl chloride solution a colloidal hydroxide has been obtained (0.6 gram zirconia in 100 c.c.) which was clear in both transmitted and reflected light. The hydrosol retains some chlorine which is not directly precipitated by silver nitrate but is protected by the colloid. On attempting to remove the last of the chlorine a hydrogel is formed. The chlorine can be precipitated after boiling with nitric acid. A largely hydrolyzed zirconium oxychloride containing 5.5 p.c. chlorine and 87 p.c. zirconia yields in water a milky solution in which acids give a precipitate. A colloid can be prepared from this solution nearly free from chlorine. The colloidal hydroxide is precipitated by such electrolytes as sodium or ammonium chloride (619).

A colloidal hydroxide has also been prepared by boiling a highly basic zirconium nitrate with water and filtering. The hydrosol is opalescent and on evaporation yields a gummy residue which swells and dissolves in water. Slightly ionizing univalent salts have no effect upon this hydrosol, but strongly ionizing salts cause coagulation. Anions of a higher valence cause precipitation. The valence of the cation is a negligible factor (512). The dialysis of a 1.5 p.c. solution of zirconium acetate gives a clear colloidal solution containing 0.45 grams of zirconia to the 100 c.c. and very little acetic acid. Towards electrolytes it behaves in the same manner as the preparation just described (611). By peptonizing zirconium hydroxide with uranyl nitrate a yellowish, milky, strongly opalescent, very stable colloidal solution is obtained (695).

It would seem that in preparing the colloid from these hydrolyzed and highly basic compounds some of the surplus of zirconium hydroxide is separated from the salt. Lottermoser (445), who apparently



used a less hydrolyzed solution, failed to secure a hydrosol. Van Bemmelen (42) advanced the theory that the zirconium hydroxide forms in these highly basic salts an adsorption compound with the zirconyl salt. It will be seen later that the hydrolysis progresses in a far-reaching manner, though halting places are observed where definite compounds seem to be formed. Müller (512) has suggested that opalescent or non-opalescent dilute solutions of zirconyl hydroxide in salts of zirconium are to be looked upon not as basic but as adsorption compounds of the colloidal hydroxide with the salt. These salts then yield colloidal solutions and in all of them a hydrogel is present. The adsorptive power of zirconium is very considerable and comparable with that of aluminum hydroxide. On this account its utilization has been proposed in the purification of water, mordanting of textiles, preparation of lac dyes, and for similar purposes.

*Hydrolysis and formation of zirconyl hydroxide.* All salts of zirconium hydrolyze very readily when dissolved in water with the separation of free acid and zirconyl hydroxide. Salts of quadrivalent zirconium do not exist in aqueous solution. In such solutions the bivalent zirconyl radical is always present. This forms a weak base and is amphoteric. Definite proof as to the formation of this hydroxide is not always available, but the ease with which the normal hydroxide is itself dehydrated, especially in even moderately warm water, and other facts render this probable. In some cases the zirconyl hydroxide has been separated by dialysis. When the acid is volatile it is easily lost on evaporation or when the solution is set aside over a caustic alkali absorbent. The hydrolysis is often progressive so that the acid constituent may be largely washed away from a precipitated insoluble basic salt. In a number of instances the insoluble basic compound is formed only after prolonged standing of the solution. This precipitation may be hastened by boiling the solution. This may indicate a progressive hydrolysis, the normal hydroxide being first formed and then dissociated into zirconyl hydroxide and water, the insoluble basic salt being a compound of zirconyl hydroxide. This being the most plausible assumption, the basic salts to be described later will have formulas ascribed to them as compounds of zirconyl hydroxide. Many of these basic compounds form crystals whose composition can be definitely determined or precipitates in which the composition is little changed by repeated washings. Some form neither crystals nor precipitates but leave a gummy mass on evaporation. In such masses indications of crystalline structure

are sometimes to be found. The custom has often been followed of reporting the basic compounds with formulas containing  $\text{ZrO}_2$ . There would seem to be little justification for the use of this or of the easily dehydrated  $\text{Zr}(\text{OH})_4$ . Some of the salts would seem to be adsorption compounds with colloidal  $\text{ZrO}(\text{OH})_2$  and lacking in definite composition.

On heating a zirconium salt of a volatile acid, such as hydrochloric or sulphuric, to a temperature of  $500^\circ$  to  $800^\circ$  most of the acid is eliminated but traces of these acids are held even after prolonged ignition (744). The amount retained is ordinarily too small to interfere materially with analytical results.

*Higher Oxides of Zirconium.* 1.  $\text{ZrO}_3$  was obtained in the hydrated form as a white precipitate by Cleve (146) on adding hydrogen peroxide to a solution of zirconium sulphate made alkaline by ammonium hydroxide. The precipitate was dried over sulphuric acid and potassium hydroxide and gave on analysis 13.12 p.c. of oxygen in excess of  $\text{ZrO}_2$ , which corresponds closely with the amount calculated for  $\text{ZrO}_3$ . Bailey (22) on repeating this experiment used an acid solution so as to avoid the possible presence of zirconium hydroxide from the excess of ammonia. He also obtained a bulky, white precipitate which, on being heated gently with hydrochloric acid and potassium iodide, liberated iodine. This precipitate, after thorough washing, was allowed to stand three months. The analysis yielded 69.46 p.c. of zirconium and 30.54 p.c. of oxygen. A freshly precipitated preparation gave closely concordant results. These correspond with the formula  $\text{Zr}_2\text{O}_5$ . Further determinations of the combined water gave the complete formula as  $\text{Zr}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ . This is partially dissociated on boiling and is insoluble in dilute sulphuric and acetic acids. From more dilute solutions the precipitate corresponded to  $\text{ZrO}_3 \cdot 5\text{H}_2\text{O}$ . If this is dried at  $100^\circ$  the analysis corresponds with  $\text{ZrO}_3$  (22).

Piccini (549) failed to get such precipitates. It has been suggested (238) that the solutions used by him were too dilute and that the compound  $\text{Zr}_2\text{O}_5$  obtained by Bailey was perhaps a decomposition product. Geisow (238) also confirmed the results of Cleve, using a 30 per cent solution of hydrogen peroxide and precipitating in solution made alkaline. Pissarjewski (554), who prepared  $\text{ZrO}_3$  (hydrated) by precipitation with  $\text{H}_2\text{O}_2$  in an ammoniacal solution at a temperature of  $0^\circ$  to  $3^\circ$ , stated that the trioxide loses active oxygen on standing and that it is entirely lost at  $75^\circ$ . The heat of formation is given as



— 21.786 cal. The formation of this precipitate with hydrogen peroxide has been recommended as a means of quantitative separation of zirconium from iron (238, 775).

The trioxide has also been prepared by the action of hydrogen peroxide on an alkali tartrate solution (775, 293); by its action upon zirconyl hydroxide or the action of sodium hypochlorite on zirconyl nitrate at 8°–10°; and by the electrolysis of an alkaline solution of sodium chloride in which zirconyl chloride is suspended (549). It forms a gelatinous precipitate which is decomposed on standing over sulphuric acid or soda lime.

### Zirconium and Nitrogen

*Zirconium Nitride.* Zirconium shows a strong affinity for nitrogen. The metal readily combines with it when heated in a stream of nitrogen or when heated in the air. Thus the earlier attempts at preparing zirconium yielded products containing the nitride, as air was not rigidly excluded. On exclusion of nitrogen no nitride was formed (818). The evidence as to the presence of nitride was the formation of ammonia on treatment with a caustic alkali. When the carbide is heated in nitrogen the carbon is displaced and a nitride formed (779). The nitrides heated in a stream of hydrogen yield ammonia and the metal (473).

The formation of the nitride was observed by Wöhler (820) in 1839. In 1859 Mallet (463) in attempting to prepare zirconium by the reduction of the oxide with aluminum in a lime crucible, which cracked, obtained a product which on treating with hydrochloric acid left undissolved iron-black, lustrous leaflets and a golden-colored substance. The latter was in the form of microscopic cubes which were slightly attacked by acids and caustic alkalis and showed a slight formation of ammonia when left under water. By heating amorphous zirconium in a stream of ammonia until the glass tube softened he obtained a product which gave off ammonia abundantly when fused with caustic alkali. Heated in the air it burned to zirconia. A similar product was prepared by heating zirconium chloride in a stream of ammonia. Zirconium heated in a stream of cyanogen gave a dark, amorphous powder which gave off ammonia abundantly on fusion with caustic alkali and burned to a white powder in air. He believed the cyanogen formed a nitride though possibly admixed with cyanide. No analyses were reported.

Matthews (473) heated  $\text{ZrCl}_4 \cdot 8\text{NH}_3$  to redness in a stream of nitrogen. Abundant fumes of ammonium chloride were given off. The residue, a pearl-gray powder, yielded ammonia when heated in a stream of hydrogen. The nitrogen present was determined by dissolving this gas in a standard solution of hydrochloric acid. The residue was burned to zirconia and weighed. The analysis corresponds with the formula  $\text{Zr}_3\text{N}_8$ . When  $\text{ZrCl}_4 \cdot 4\text{NH}_3$  was treated in the same way the analysis of the product gave  $\text{Zr}_2\text{N}_3$ .

Wedekind (777) found that when magnesium was heated in the air with zirconia a greenish-brown crystalline powder was left. This glowed on gentle heating and when scattered in a flame burned with scintillations. It was notably stable towards acids, excepting hydrofluoric, and did not conduct electricity. On fusing with alkalis ammonia was given off. The analysis corresponded with the formula  $\text{Zr}_2\text{N}_3$ .

Bruyère and Chauvenet (110) have shown that all ammonia compounds with zirconium tetrachloride yield  $\text{Zr}(\text{NH}_3)_4\text{Cl}_4$  on heating up to  $195^\circ$ . This is true also of the iodide. At higher temperatures the halogen acid and not ammonia is given off. Thus at  $225^\circ$ – $250^\circ$  the amide  $\text{Zr}(\text{NH}_2)_4$  is formed in an atmosphere of hydrogen or ammonia. Above  $250^\circ$  the product seems to be a mixture of an imide and a nitride,  $\text{Zr}(\text{NH})_2 + \text{Zr}_3\text{N}_4$ . At  $350^\circ$  only the  $\text{Zr}_3\text{N}_4$  remains. This is insoluble and unchanged in water. According to these observers the nitride,  $\text{Zr}_3\text{N}_8$ , reported by Matthews is to be regarded as a mixture of the amide  $\text{Zr}(\text{NH}_2)_4$  and the imide  $\text{Zr}(\text{NH})_2$ .

Wedekind (785), in examining the properties of the purest zirconium he could obtain, found that nitrogen shows little action upon powdered zirconium under  $1000^\circ$ . There is practically no change at  $500^\circ$ ; at  $700^\circ$  1 p.c. is changed; at  $800^\circ$  4 p.c.; at  $1050^\circ$  to  $1080^\circ$  9 p.c. The product at this temperature is  $\text{Zr}_3\text{N}_2$ . The same nitride is given by ammonia at  $1000^\circ$ . It is a crystalline powder with metallic lustre, more resistant to oxygen and chlorine than zirconium, with about the same resistance to acids. Solutions of alkalis show no action, but fusion with caustic alkalis yields ammonia. It is stable when heated in a hydrogen stream up to  $1000^\circ$ . It conducts electricity.

Curtius (157) has stated that on adding a solution of sodium azide ( $\text{NaN}_3$ ) to a solution of zirconium sulphate a precipitate of zirconium hydroxide is formed and no zirconium is left in the filtrate. The azide was not formed by this method.



The nitrides reported are  $Zr_3N_2$ ,  $Zr_2N_3$ ,  $Zr_3N_4$ , and  $Zr_3N_8$ . In addition there are the amide  $Zr(NH_2)_4$  and the imide  $Zr(NH)_2$ .

### Zirconium and Carbon

*Zirconium Carbide.* The first observation as to the formation of zirconium carbide was made by Berzelius, who, in preparing zirconium by means of potassium containing carbon, obtained amorphous zirconium which left a residue of carbon on treatment with boiling hydrochloric acid and gave off an unpleasant-smelling gas containing hydrogen.

Troost (714) heated powdered zircon with carbon in an electric furnace, using a current of 35 amperes at 70 volts, and obtained metallic-like masses of carbide. The analyses indicated the composition  $ZrC_2$  but did not agree closely and no distinction seems to have been made between mixed and combined carbon. The product did not alter in the air and was not attacked by water or acids except hydrofluoric. If little carbon was used the product did not oxidize at red heat in the air. If much carbon was used in its preparation it burned brilliantly.

Moissan (500), on fusing powdered zirconia in an electric furnace with an excess of carbon, prepared a substance containing 4 to 5 p.c. of carbon. When this was heated with more zirconia the carbon was eliminated. When rich in carbon it was rapidly decomposed by air. Later (501) he mixed the powdered zirconia with carbon prepared from sugar, using oil and pressing the mass into a cylinder which was then calcined. It was afterwards subjected to the action of a current of 1000 amperes and 50 volts. Varying amounts of carbon were used, yielding the same results. The product had a metallic appearance and was unchanged in moist air even when heated to  $100^\circ$ . The analysis yielded 88.6 p.c. of zirconium and 11.4 p.c. of carbon, which agrees with the formula  $ZrC$ . The fact that this composition was maintained when the amount of carbon used was varied brings still more into question the existence of the  $ZrC_2$  reported by Troost. Wedekind (785) obtained the same result as Moissan by using a current of 600 amperes, voltage not given.

The carbide has a hardness between 7 and 9, scratching glass and quartz, and its use as an abrasive has been suggested. Chlorine acts upon it at  $250^\circ$ , bromine at  $300^\circ$ , and iodine at  $400^\circ$ . At a red heat it burns in the air. Sulphur yields a small amount of the sulphide

when heated with this carbide to a red heat. If melted with carbon in an electric furnace carbon is dissolved, the excess separating as graphite on cooling. Ammonia and water are without action at a red heat. Hydrofluoric acid acts readily in the cold. Boiling hydrochloric acid has no action. Nitric acid acts slightly when dilute, but the concentrated acid acts immediately and violently and so does aqua regia. Sulphuric acid readily decomposes it when heated. Nitrates and permanganates attack it readily, and chlorates give an explosive mixture when heated. Fused caustic potash dissolves it readily. There is no action on fusing with potassium cyanide.

Wedekind (779) prepared a carbide from native zirconia by mixing the finely-ground powder with carbon and heating in an electric furnace. The product sintered into a metallic-like mass which was stable in air, water, and hydrochloric acid but was decomposed by chlorine at 300°. It was found to contain a small percentage of iron oxide, silica, and silicates. After deducting this the analysis agreed well with the formula  $ZrC$ . It is a good conductor of electricity and its use for electrodes has been suggested. As anode it would be quickly attacked by oxygen. When heated to a red heat in a stream of nitrogen a nitride was formed. Mott (509) has given the boiling point of the carbide as 5100°.

### Zirconium and Sulphur

*Zirconium Sulphide.* The sulphide was first prepared by Berzelius (53) by heating the metal with sulphur in a vessel previously evacuated. When the two were heated in hydrogen there was a slight appearance of flame. No details are given as to the composition of the product but the impurities in the metal used would necessarily render it impure. The sulphide is described as a dark cinnamon-brown powder which could not be polished to a lustrous appearance. As will be seen later, the pure sulphide is crystalline and has a steel-gray color. When fused with caustic potash zirconia and potassium sulphide were formed. Hydrofluoric acid dissolved it easily with the evolution of hydrogen sulphide. Boiling aqua regia dissolved it slowly. Hydrochloric, nitric, and sulphuric acids, as well as a solution of caustic potash, gave no reaction.

Paykull (536) prepared an impure sulphide (containing some oxygen) by subliming zirconium tetrachloride in a stream of hydrogen sulphide, the presence of oxygen not being entirely excluded. The



product was stable in the air and water and burned, when heated, with the formation of sulphur dioxide. It was oxidized by aqua regia and also by nitric acid. Chlorine gave zirconium tetrachloride and sulphur dioxide on the application of heat. Moissan and Lengfeld (501) obtained a small amount of the sulphide on heating zirconium carbide and sulphur to a dark red heat. Fremy (231), by the action of carbon bisulphide upon zirconia at a red heat, prepared zirconium sulphide in the form of fine, needlelike crystals of a steel-gray color. These showed the characteristics of the product obtained by Berzelius. They were not decomposed by water nor ordinary acids except nitric acid, which oxidized the zirconium readily, giving an abundant deposit of sulphur. The formula for the sulphide prepared by these methods would seem to be  $\text{ZrS}_2$ . Hauser (294) repeated the preparation by the method of Berzelius by heating the metal in the vapor of sulphur, but in this case also the metal was not pure.

*Zirconium Oxysulphide.* The oxysulphide,  $\text{ZrOS}$ , was also prepared by Hauser (294) by the reduction of the sulphate (dried at  $400^\circ$ ) when heated to a strong red heat in a stream of dry hydrogen sulphide. It is a bright yellow powder with a density of 4.87. If removed from the tube before completely cooling it caught on fire. The analysis (Zr, 65.3 p.c. and S, 22.8 p.c.) agrees with the formula  $\text{ZrOS}$ .

### Zirconium and Boron

*Zirconium Boride.* The boride has been prepared by Tucker and Moody (723), who used zirconium gotten by the reduction of the double fluoride of potassium and zirconium by means of aluminum. Hence their results are impaired by the presence of aluminum as an impurity. Fifteen grams of this product were heated with 2.2 grams of boron in a carbon crucible for five minutes by a current of 200 amperes at 65 volts. The product was brittle, steel-gray in color, and under the microscope appeared as an agglomeration of brilliant, translucent to transparent, tabular crystals having a density of 3.7 and a hardness of 8. They were slowly attacked by hot concentrated acid and aqua regia. The analysis gave 86 p.c. of zirconium, which would point to the formula  $\text{Zr}_3\text{B}_4$  if these two elements alone were present.

Wedekind (773) tried the reduction of zirconia by means of boron, heating 5 grams of zirconia with 1.1 grams of boron in an electric furnace. This yielded a mass which was not homogeneous, which scratched glass, and which was fairly stable to hot water.

Dilute hydrochloric acid evolved a gas, burning with an almost colorless flame and darkening paper soaked in silver nitrate solution. The gas was probably hydrogen with some boron hydride. Concentrated sulphuric acid was reduced, evolving sulphur dioxide. When the experiment was repeated at a higher temperature and a more prolonged exposure there was formed a gray-black mass which was acted upon by hydrochloric acid only on strong boiling. The gas formed burned with a green flame. The mass was not acted upon by sulphuric acid in the cold but evolved sulphur dioxide on strong heating, which would happen if free carbon was present. Dark crystals were formed when the mass was dissolved in melted copper and allowed to cool. On analyzing the original mass it was found to contain 30.16 p.c. of carbon and 57.9 p.c. of zirconium. If the carbon is regarded as admixed and the zirconium is calculated carbon-free, the percentage of zirconium becomes 82.8 and this approximates the required percentage in  $\text{Zr}_3\text{B}_4$ . The product may be regarded as a boride mixed with carbon or as a borocarbide. The experiments do not afford a satisfactory basis for a decision.

### Zirconium and Silicon

*Zirconium Silicide.* The preparation of the silicide by the action of silicon upon zirconia was tried by Wedekind (773) with only partial success. When the silicon was added in accordance with the equation  $\text{ZrO}_2 + \text{Si} = \text{SiO}_2 + \text{Zr}$  and heated in an electric furnace a dark, compact mass containing undecomposed zirconia was formed. With an excess of silicon the regulus had a metallic lustre with crystalline fracture. The broken surface showed silvery crystals. These crystals were very resistant to chemical action and recrystallized on sublimation. By mixing equivalent weights of zirconium and silicon and heating in vacuum to  $1000^\circ$ – $1200^\circ$  a homogeneous, gray, slightly-sintered powder was obtained (791). Treating this with warm caustic potash excess silicon was removed and the silicide remained.

Hönigschmid (354) has prepared the silicide by heating in a Perrot furnace a mixture of potassium fluosilicate (120 grams), the double silicate of potassium and zirconium (15 grams), and aluminum (50 grams). The product was in the form of very brilliant metallic crystals, which were separated from aluminum and silicon by alternate treatment with hydrochloric acid and a solution of potassium hydroxide. The crystals still retained a small amount of aluminum—some



2 or 3 p.c.—due doubtless to the formation of a zirconium-aluminum alloy. These crystals were small and of a clear iron-gray color. They formed rhombic columns with a prism of  $58^{\circ} 30'$  terminated by a longitudinal and a transverse dome. The density was 4.88 and the hardness approximately that of felspar. They remained unaltered in air. When heated on platinum foil they were apparently unchanged but burned if previously ground to a fine powder. When the products of combustion were treated with hydrofluoric acid a brown residue of amorphous silicon was left. Heated in oxygen the crystals burned readily, forming silica and zirconia. Fluorine acted upon them at a slightly elevated temperature with the appearance of a flame. Chlorine attacked them at a red heat, and bromine and iodine only at a high temperature but without incandescence. Ordinary acids were without action, except hydrofluoric acid, which dissolved them with the liberation of hydrogen. Solutions of alkaline hydroxide were without action, but when fused in alkali hydroxides they were readily decomposed. Potassium bisulphate showed no action.

By using the thermite process Hönigschmid (354, 355) obtained still better results. Pure, iron-free sand (180 grams) was mixed with zirconia (20 grams), sulphur (250 grams), and pure aluminum (200 grams) in a Hessian crucible, covered with magnesium powder, and ignited. It was heated to a white heat. The silicon and silicide collected at the bottom of the crucible. After cooling this regulus was separated from the aluminum sulphide, broken up and powdered, and then treated alternately with hydrochloric acid and 10 p.c. potassium hydroxide solution in a water bath. The aluminum and silicon dissolved and analysis showed much less aluminum retained. The zirconium silicide prepared in this way was identical in properties and composition with that obtained in the Perrot furnace. The analysis gave zirconium 61.8 p.c. and silicon 38.2 p.c. with a trace of aluminum. The formula, therefore, is  $\text{ZrSi}_2$ . Wedekind and Pintsch have patented a process for the commercial preparation of the silicide (791).

### Zirconium and Phosphorus

*Zirconium Phosphide.* Gewecke (243) has prepared zirconium phosphide by subliming zirconium tetrachloride in an atmosphere of phosphine. The reaction was carried out in a piece of glass tubing. The properties of the phosphide are closely parallel to those of the corresponding titanium compound prepared by the same method.

It is a gray, glistening substance somewhat like the hammer scales from copper. The density is 4.77 and it is hard and brittle. It is stable in air and unaffected by water. The phosphide resists ordinary chemical reagents and conducts electricity. The analysis showed 40.18 p.c. of phosphorus and 59.78 p.c. of zirconium, which agrees with the percentages calculated for  $\text{ZrP}_2$ .

Attempts at preparing the phosphide by subliming the zirconium tetrachloride over potassium phosphide in a stream of hydrogen failed to yield a definite compound with constant proportions. An energetic reaction took place with appearance of flame, and there was left a black mass out of which potassium chloride was leached with water. A graphite-like substance was left and this was found to contain some oxygen.



## Chapter IV

### Compounds with the Halogens and Their Acids

#### Zirconium and Fluorine

*Zirconium Fluoride.* Zirconium fluoride,  $\text{ZrF}_4$ , was first prepared by Berzelius (50) by dissolving zirconia in hydrofluoric acid until the liquid gave none or only a slightly acid taste. Crystals were obtained by evaporating the solution. He stated that the crystalline salt was resolved by water into an acid salt and a basic salt, the latter being insoluble. On boiling the solution a partial precipitation took place and the liquid became more acid. The hydrolysis of zirconium salts in aqueous solution was thus distinctly recognized and the accompanying phenomena recorded with the accustomed care and accuracy of the great master. The crystalline substance reported by Berzelius as easily soluble was unquestionably the hydrate  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ , as  $\text{ZrF}_4$  is only slightly soluble. According to his view of the composition of the oxide, namely,  $\text{Zr}_2\text{O}_3$ , his formula for the fluoride would be given as  $\text{Zr}_2\text{F}_3$ .

Dewille (181) prepared the fluoride by treating with hydrogen chloride a mixture of powdered zircon and fluospar placed in a carbon boat and enclosed in a carbon tube. He obtained colorless, transparent crystals, apparently belonging to the hexagonal system but imperfectly formed. The small crystals were hard to measure. He reported them as insoluble in water, not attacked by acids, and volatile at a white heat. Later, in conjunction with Caron (184) he prepared the fluoride by passing hydrogen fluoride over powdered zircon heated to a white heat in a carbon crucible.

Marignac (468) obtained the anhydrous fluoride by heating zirconia with ammonium fluoride or ammonium-zirconium fluoride. Wolter (824) prepared the fluoride by heating the ammonium-zirconium fluoride,  $2\text{NH}_4\text{F} \cdot \text{ZrF}_4$ , driving off the ammonium fluoride, and purifying the zirconium fluoride by sublimation in a stream of hydrogen. A still better method used by him depended upon the double decomposition taking place between zirconium tetrachloride and hy-

drogen fluoride, both carefully freed from water and heated in a tube. The analysis agreed with the formula  $\text{ZrF}_4$ . On subliming small, strongly refracting crystals were obtained having a density of 4.43 at  $16^\circ$ . The molecular weight at  $1200^\circ$  was 166.1. It was found that 1.388 grams dissolved in 100 c.c. of water at ordinary temperature without visible change. At  $50^\circ$  hydrolysis took place and a white precipitate formed. The only hydrate obtained agreed with the formula  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ . With liquid ammonia a white pulverulent compound was formed, having the composition  $5\text{ZrF}_4 \cdot 2\text{NH}_3$ . Gaseous ammonia showed no action, nor does this fluoride combine with pyridin and similar organic substances as does the tetrachloride. Furthermore, it has much less power of uniting with other substances than its isomorphs, titanium tetrafluoride and stannic tetrafluoride. This Wolter attributed to the small molecular volume, 37.5, as compared with 44.3 for  $\text{TiF}_4$  and 40.7 for  $\text{SnF}_4$ , having the same number of atoms condensed in a smaller volume and hence less freedom of motion.

Zirconium fluoride, if not too strongly ignited, is readily soluble in water. Crystals form on gently evaporating this solution acidulated with hydrofluoric acid. These crystals, which have a composition equivalent to  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ , can be redissolved and recrystallized without change. On account of this fact it has been maintained that the fluoride does not undergo hydrolysis, overlooking the early experiments of Berzelius which indicate clearly an hydrolysis.

Chauvenet (127) has made a study of the supposed compound  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$  and has come to the conclusion that it is more probably a derivative of zirconyl and has the composition  $\text{ZrOF}_2 \cdot \text{H}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ , a rearrangement of the same atoms in the molecule. It is stable in air and in vacuo but begins to lose water at  $100^\circ$ . At  $140^\circ$  it has the composition  $\text{ZrOF}_2 \cdot \text{H}_2\text{F}_2$  but above this temperature it loses hydrofluoric acid and becomes  $\text{ZrOF}_2$ . This compound recombines with hydrofluoric acid when placed in the cold acid and regains its former composition. In other words, the fluoride behaves in its action towards water as the salts of the other halogen acids do. The residue left on complete drying and calcination of the crystals is zirconia, though it probably retains traces of fluorine.

Wedekind (784) has observed that in igniting zirconia with hydrofluoric acid to remove such silica as may be present there is a loss of part of the zirconia. This loss also occurs when a mixture of hydrofluoric acid and dilute sulphuric acid is used but may be prevented by using the sulphuric acid in excess. In the latter case all of the



fluorine is expelled from combination with the zirconium. If no excess is present,  $\text{ZrF}_4$ , which is volatile at the temperature of ignition, may be formed.

*Zirconium Double Fluorides or Fluozirconates.* Conclusive evidence is lacking to decide whether the numerous double fluorides formed by zirconium are true fluorzirconates or not. On the basis of Chauvenet's work already cited some are zirconyl fluorides, and in the following description these will be classified as such. The fluorides and double fluorides of zirconium are, in general, isomorphous with those of the analogous elements, silicon, titanium, and tin (stannic), and Gossner (251, 252) has reported certain regularities existing between these compounds. For example, the double fluorides formed with zinc fluoride show the following gradations in density.

	$\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$	$\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$	$\text{ZnZrF}_6 \cdot 6\text{H}_2\text{O}$	$\text{ZnSnF}_6 \cdot 6\text{H}_2\text{O}$
Sp. Gr.	2.139	2.106	2.258	2.445

The independent existence of a fluorzirconic acid,  $\text{H}_2\text{ZrF}_6$ , however, has not as yet been proved.

### Double Fluorides of Univalent Elements

*Lithium.* Two of these double fluorides have been prepared with the proportions 2 : 1 and 4 : 1 +  $2/3 \text{ H}_2\text{O}$ .

$2\text{LiF} \cdot \text{ZrF}_4$  or  $\text{Li}_2\text{ZrF}_6$ , Wells and Foote (809). When lithium fluoride (0.7-2.0 grams) is added to zirconium fluoride (20 grams) hexagonal crystals are formed, showing prism and pyramid and rarely a basal plane. Separate preparations were analyzed, yielding results in accord with the above formula. This is the normal lithium fluozirconate  $\text{Li}_2\text{ZrF}_6$ .

$4\text{LiF} \cdot \text{ZrF}_4 \cdot 2/3\text{H}_2\text{O}$  (809). This salt is formed when the above salt is recrystallized. It also forms when lithium fluoride (5-7 grams) is mixed with zirconium fluoride (20 grams). It forms a crust of very small crystals which appear under the microscope to be homogeneous. In one preparation these crystals were mixed with the 2 : 1 variety. Both hot and cold solutions were used. On recrystallizing the small crystals were partially dissociated and some lithium fluoride crystallized out. As lithium fluoride is very insoluble only a comparatively small amount is dissolved in the solution of zirconium fluoride. Hence there is a tendency for the lithium fluoride to separate and the 2 : 1 salt to form. Also, the observations reported and

the divergences in the analyses throw doubt upon the homogeneity of the substance. Neglecting the water, it may be written  $2\text{LiF} \cdot \text{ZrF}_4$ . The zirconium fluoride used in the above experiments and in all that follows is of course the hydrated one, and it must be borne in mind that doubt exists as to its exact nature, especially as to whether or not it is a derivative of the zirconyl radical. If Chauvenet is justified in looking upon it as a zirconyl derivative, the analysis would tend to prove that under the influence of a stable fluoride readjustment takes place. It must be noted that some of these salts are reported as giving off hydrofluoric acid after the water had been driven off.

*Sodium.* Two double fluorides are known, both anhydrous, with the proportions 2 : 1, 5 : 2.

$2\text{NaF} \cdot \text{ZrF}_4$  (760). When from one to two parts of sodium fluoride are added to fourteen parts of zirconium fluoride a crust of minute crystals of hexagonal outline, which do not recrystallize, is formed. From 0.5 to 2 p.c. of water, supposed to be mechanically included, was found in the analysis. The fluorine was estimated by difference. This would correspond to the normal fluorzirconate,  $\text{Na}_2\text{ZrF}_6$ .

$5\text{NaF} \cdot 2\text{ZrF}_4$  (468, 809). This salt was formed under widely varying conditions on dissolving together the two fluorides, also (468) by double decomposition between sodium chloride and ammonium-zirconium fluoride. The crystals are described as showing good, sharp forms but very small. They appear distinctly orthorhombic in habit, consisting in the main of rather stout prisms made up of two prismatic planes and terminated by a rather steep brachydome. In another habit, which is rarer, the front pinacoid is broadly developed, while the prisms are very small. This type also shows at times a pyramid. The plane of the optic axes lies in the base. The optic angle is large. The double refraction is very low. In their form the crystals strongly recall the figures of chrysolite (olivine). No loss of weight was detected on heating, hence no water was present. There was also no loss of weight at red heat. The fluorine was estimated by difference. This salt may be written  $\text{NaF} \cdot 2\text{Na}_2\text{ZrF}_6$ .

*Ammonium.* Two double fluorides have been reported 2 : 1 and 3 : 1, both anhydrous.

$2\text{NH}_4\text{F} \cdot \text{ZrF}_4$ , Marignac (468). This salt was formed from the solution of the two fluorides. It exists in two modifications, Gossner (251). First, hexagonal crystals which are formed on the complete evaporation of the solution. These are thin, tabular, with very per-



fect cleavage, and optically are weakly negative. Second, rhombic bi-pyramidal crystals, separate before the hexagonal in the earlier stage of the evaporation. These are isomorphous with the corresponding potassium salt. This compound is unchanged on heating to  $100^{\circ}$ . On stronger heating ammonium fluoride is lost and  $\text{ZrF}_4$  is left which forms  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$  on dissolving in water. This is the normal fluo-zirconate,  $(\text{NH}_4)_2\text{ZrF}_6$ .

$3\text{NH}_4\text{F} \cdot \text{ZrF}_4$ , Marignac (468). This salt is formed when a large excess of ammonium fluoride is used. It forms regular octahedra and cubic octahedra with simple refraction. When heated to  $100^{\circ}$  it is unchanged. The last two ammonium double fluorides, as well as the analogous potassium salts, have the same composition as those of titanium but are not isomorphous. This salt may be written  $\text{NH}_4\text{F} \cdot (\text{NH}_4)_2\text{ZrF}_6$ .

*Potassium.* Three double fluorides are known—1 : 1 :  $\text{H}_2\text{O}$ , 2 : 1, 3 : 1.

$\text{KF} \cdot \text{ZrF}_4 \cdot \text{H}_2\text{O}$ , Marignac (468). This salt is formed only in the presence of a large excess of zirconium fluoride. It is decomposed on re-solution in water. This solution causes no effervescence on the addition of ammonium carbonate. The water of crystallization is lost at  $100^{\circ}$ . Heated beyond this temperature hydrofluoric acid escapes. The crystals are monoclinic prisms or imperfectly formed, short prisms, the angle values showing a wide range. This appears to be a zirconyl salt and may be written  $\text{KF} \cdot \text{ZrOF}_2 \cdot \text{H}_2\text{F}_2$ .

$2\text{KF} \cdot \text{ZrF}_4$  (53, 468). This is formed when equivalent parts of potassium fluoride and zirconium fluoride are mixed. The crystals are rhombic pyramidal, generally acicular but showing variations. This salt can be heated up to a red heat without loss of weight. At a red heat it melts to a paste, giving off hydrofluoric acid, which Marignac attributed to the moisture in the air. An instructive fact lies in the rapidly increasing solubility in water with rise of temperature. One hundred c.c. of water at  $0^{\circ}$  dissolves 0.781 grams; at  $15^{\circ}$ , 1.41 grams; at  $19^{\circ}$ , 1.69 grams; at  $100^{\circ}$ , 25.00 grams. On cooling a boiling solution a mass of fine needlelike crystals is formed. If a less concentrated solution is cooled slowly the crystals obtained are not in a determinable form.

The salt was purified by numerous recrystallizations and several analyses made by the usual method adopted by Marignac of adding sulphuric acid, igniting, and weighing the zirconia from which the potassium sulphate had been leached. In the filtrate the potassium

sulphate was determined but the fluorine was calculated from the amount necessary to combine with the potassium and zirconium. The formula may be written  $K_2ZrF_6$ , the normal fluozirconate.

$3KF.ZrF_4$ . This salt is formed when an excess of potassium fluoride is used. The crystals are in the form of small, regular octahedra and cubic octahedra, usually the first. Not only do the crystal angles agree with those of the regular system but they show no double refraction. They decrepitate on heating to a red heat, but if previously pulverized and dried they suffer no loss of weight. The analyses of Marignac (468) and Berzelius (53) agree as to their composition. The formula may be written  $KF.K_2ZrF_6$ .

In preparing these three compounds then the first is formed in the presence of an excess of zirconium fluoride, the last when the potassium fluoride is in excess, and the second when the proportions lie between these two extremes.

*Rubidium.* Two double fluorides are known in the proportions 2 : 1 and 3 : 1.

$2RbF.ZrF_4$ . Behrens (37) prepared this salt by adding rubidium chloride to a solution of zirconium sulphate to which ammonium fluoride and free hydrofluoric acid had been added. The salt crystallizes in right-angle prisms. This is the normal fluozirconate  $Rb_2ZrF_6$ .

$3RbF.ZrF_4$ . This compound is formed when the proportions in the mixture are changed and crystallizes in strongly refracting octahedra. The formation of these salts was used by Behrens in his microchemical reactions for detecting rubidium. The formula may be written  $RbF.Rb_2ZrF_6$ .

*Cæsium.* Three double fluorides are known, with the proportions 2 : 1, 1 : 1 :  $H_2O$ , and 2 : 3 :  $2H_2O$ . Wells and Foote (808) have prepared these salts by mixing the solutions of the respective fluorides in varying proportions and adding more or less of hydrofluoric acid to the sufficiently concentrated solution.

$2CsF.ZrF_4$ . By the use of an excess of cæsium fluoride this salt was formed even when small amounts of zirconium fluoride were present. It crystallizes in large plane hexagonal tables, exhibits negative double refraction, and can be recrystallized without change. This is the normal fluozirconate  $Cs_2ZrF_6$ .

$CsF.ZrF_4.H_2O$ . This salt is obtained by using larger proportions of zirconium fluoride than in the preparation of the foregoing compound. Monoclinic crystals are formed which also recrystallize without change.



$2\text{CsF} \cdot 3\text{ZrF}_4 \cdot 2\text{H}_2\text{O}$ . When a large excess of zirconium fluoride was used very small, difficultly-soluble crystals separated out. These were too small to determine crystallographically but showed some action upon polarized light. On recrystallization they were partially changed into the 1 : 1 compound. In analyzing these salts all of the constituents were determined. This salt may be written  $\text{Cs}_2\text{ZrF}_6 \cdot 2(\text{ZrOF}_2 \cdot \text{H}_2\text{F}_2)$ .

*Thallium.* Thallium (809) forms four double fluorides or fluozirconates having the proportions 1 : 1, 1 : 1 :  $\text{H}_2\text{O}$ , 5 : 3 :  $\text{H}_2\text{O}$ , and 3 : 1.

$\text{TlF} \cdot \text{ZrF}_4$  and  $\text{TlF} \cdot \text{ZrF}_4 \cdot \text{H}_2\text{O}$ . When one part of thallium fluoride is added to a concentrated solution of three or four parts of zirconium fluoride needlelike crystals are formed containing one molecule of water if the solution is cooled before crystallization. When the solution is evaporated until crystallization begins and then cooled the anhydrous salt is deposited in minute square plates. On recrystallizing the salt of the 5 : 3 types, having the composition  $5\text{TlF} \cdot 3\text{ZrF}_4 \cdot \text{H}_2\text{O}$ , is deposited. This salt crystallizes in needles when one to three and a half parts of thallium fluoride are added to a solution of one part of zirconium fluoride. If as much as four parts of thallium fluoride are used the same salt crystallizes in prisms of hexagonal outline, which under the microscope are seen to be twinned, and in this respect resemble the hexagonal-shaped crystals of aragonite. On recrystallization both give the needle-shaped crystals. Analyses of the different forms show that they have the same composition.

$3\text{TlF} \cdot \text{ZrF}_4$ . This compound crystallizes in brilliant octahedra when the solution of four to twenty parts of thallium fluoride are added to a solution of one part of zirconium fluoride. It recrystallizes without change. The following formulas may be ascribed to these various compounds: (1)  $\text{TlF} \cdot \text{ZrF}_4$ ; (2)  $\text{TlF} \cdot \text{ZrOF}_2 \cdot \text{H}_2\text{F}_2$ ; (3)  $\text{TlF} \cdot 2\text{Tl}_2\text{ZrF}_6 \cdot \text{ZrOF}_2 \cdot \text{H}_2\text{F}_2$ ; (4)  $\text{TlF} \cdot \text{Tl}_2\text{ZrF}_6$ .

The compounds formed with the univalent metals fall into several types. First, there is the normal fluozirconate,  $\text{M}_2\text{ZrF}_6$ . This may crystallize with a molecule of the alkali fluoride,  $\text{MF} \cdot \text{M}_2\text{ZrF}_6$ . With potassium, cesium, and thallium zirconyl fluoride may enter into the composition. Thus we have  $\text{KF} \cdot \text{ZrOF}_2 \cdot \text{H}_2\text{F}_2$ ,  $\text{Cs}_2\text{ZrF}_6 \cdot 2(\text{ZrOF}_2 \cdot \text{H}_2\text{F}_2)$ , and  $\text{TlF} \cdot \text{ZrOF}_2 \cdot \text{H}_2\text{F}_2$ , and lastly  $\text{TlF} \cdot 2\text{Tl}_2\text{ZrF}_6 \cdot \text{ZrOF}_2 \cdot \text{H}_2\text{F}_2$ .

*Double Fluorides with the Bivalent Elements.* All of these compounds crystallize with water of crystallization.

*Copper.* Two double fluorides have been prepared having the proportions 3 : 2 : 16H<sub>2</sub>O, and 2 : 1 : 12H<sub>2</sub>O.

3CuF<sub>2</sub>.2ZrF<sub>4</sub>.16H<sub>2</sub>O. This salt was obtained by Marignac (468) on adding an excess of zirconium fluoride to a solution of copper fluoride prepared by dissolving copper carbonate in hydrofluoric acid. On evaporation there were formed large crystals of the double fluoride accompanied by a pale blue crust, which was almost insoluble in water and which seemed to be zirconium fluoride impregnated with the copper salt. The water of crystallization in the large crystals is lost on heating. These crystals form oblique, rhombic prisms of a beautiful blue color.

2CuF<sub>2</sub>.ZrF<sub>4</sub>.12H<sub>2</sub>O. This salt formed on adding copper fluoride to the preceding compound (468). It dissolved easily in cold water without change but was dissociated on boiling the solution, depositing crystals of copper fluoride and afterwards those of the 3 : 2 : 16H<sub>2</sub>O compound. The original crystals, of a beautiful blue color, are in the form of oblique, rhombic prisms and are isomorphous with the analogous double fluorides of zinc and nickel, though the angles differ slightly.

*Magnesium.* One double fluoride is known, with the proportion 1 : 1 : 5H<sub>2</sub>O.

MgF<sub>2</sub>.ZrF<sub>4</sub>.5H<sub>2</sub>O. This salt was prepared by Marignac (468) by the action of magnesia upon an acid solution of zirconium fluoride. There is an abundant deposit of the double fluoride mixed with much magnesium fluoride. The double fluoride is not very soluble in water, as the two salts may be separated by their relative solubilities. Crystals of the double fluoride can be gotten by the gentle evaporation of their solution. These crystals are small and generally form in oblique rhombohedral prisms. Often crystals are found which recall the transposed octahedra of the regular system as seen in spinelle. The crystals are isomorphous with the corresponding double fluoride of manganese. They have also been described by Groth (265) as small, brilliant, six-sided monoclinic tables with bent faces. The salt is completely decomposed by prolonged heating, leaving a residue of zirconia and magnesia.

*Calcium, Strontium, and Barium.* These failed to give well-defined compounds (468), which may be attributed to their insolubility, so that they could not be purified by crystallization. When the carbonate of one of the above elements was added to an acid solution of zirconium fluoride the carbonate was decomposed and an insoluble



precipitate, which was a mixture of the double fluorides and the zirconium fluoride, was formed. When barium chloride was added to a solution of potassium-zirconium fluoride a precipitate formed immediately. The analysis of the precipitate pointed to the formula  $3\text{BaF}_2 \cdot 2\text{ZrF}_4 \cdot 2\text{H}_2\text{O}$ , but no decision could be reached as to whether it was a compound or a mixture. Similar insoluble precipitates were obtained in the case of calcium and strontium.

A similar insoluble precipitate was obtained (468) in the case of lead. Some of the salt, however, went into solution and a granular, somewhat crystalline deposit was obtained on evaporation. This was decomposed by water and more rapidly by hydrofluoric acid, which precipitated lead fluoride. Other than this no distinct crystallization was observed. The method of preparation used was to add lead carbonate to an acid solution of zirconium fluoride and evaporate the liquid.

*Zinc.* Two double fluorides have been prepared with the proportions  $1 : 1 : 6 \text{ H}_2\text{O}$  and  $2 : 1 : 12 \text{ H}_2\text{O}$ .

$\text{ZnF}_2 \cdot \text{ZrF}_4 \cdot 6\text{H}_2\text{O}$ . Details are lacking as to the formation of this salt (468, 265, 252). Apparently solutions containing equivalent parts of the two fluorides were used in its preparation. It recrystallizes in long, hexagonal prisms terminating in rhombohedra. It is isomorphous with the corresponding compounds of silicon and tin (stannic) and the analogous chlorides of tin and platinum. It presents an easy cleavage along the hexagonal faces and is very soluble in water. On heating it is decomposed into the oxides of zinc and zirconium. The zinc oxide is removed with difficulty and only imperfectly by treatment with concentrated hydrochloric acid.

$2\text{ZnF}_2 \cdot \text{ZrF}_4 \cdot 12 \text{ H}_2\text{O}$ . When an excess of zinc fluoride is used this salt crystallizes out. It dissolves easily in cold water but is partially decomposed by boiling, depositing zinc fluoride. The crystals are monoclinic prisms and are isomorphous with the corresponding compound of nickel. The crystals are usually twinned.

*Cadmium.* Two double fluorides have been prepared with the proportions  $1 : 2 : 6\text{H}_2\text{O}$  and  $2 : 1 : 6\text{H}_2\text{O}$  (468).

$\text{CdF}_2 \cdot 2\text{ZrF}_4 \cdot 6\text{H}_2\text{O}$ . This salt crystallizes from a solution of the two fluorides where the zirconium fluoride is in excess. On evaporation there were formed lamellated crystals whose exact habit was not determined. Efforts at forming the salt  $\text{CdF}_2 \cdot \text{ZrF}_4 \cdot 6\text{H}_2\text{O}$  failed.

$2\text{CdF}_2 \cdot \text{ZrF}_4 \cdot 6\text{H}_2\text{O}$ . Crystals of this salt are monoclinic prisms,

isomorphous with the preceding salt and with the corresponding salt of manganese. It can be recrystallized without change.

*Manganese.* Two double fluorides are known with the proportions 1 : 1 : 5H<sub>2</sub>O and 2 : 1 : 6H<sub>2</sub>O (468).

MnF<sub>2</sub>.ZrF<sub>4</sub>.5H<sub>2</sub>O. This salt is formed when manganese carbonate is added to an acid solution of zirconium fluoride. The crystals are monoclinic prisms and isomorphous with the magnesium compound. The cleavage is imperfect and the crystals are sometimes tabular and sometimes twinned.

2MnF<sub>2</sub>.ZrF<sub>4</sub>.6H<sub>2</sub>O (468). When an excess of manganese carbonate and hydrofluoric acid are added to a solution of the preceding salt short, thick prisms (monoclinic) of this compound are formed. The cleavage is easy. These crystals dissolve in cold water without decomposition and do not decompose on boiling the solution. If, however, they are treated immediately with hot water they decompose and form an abundant deposit of manganese fluoride.

*Nickel.* Two double fluorides are formed with the proportions 1 : 1 : 6H<sub>2</sub>O and 2 : 1 : 12H<sub>2</sub>O (468).

NiF<sub>2</sub>.ZrF<sub>4</sub>.6H<sub>2</sub>O. This salt is identical with the fluorsilicate and fluostannate of nickel and completely resembles also the corresponding double fluoride of zinc except as to color, which is green. It crystallizes in regular, hexagonal prisms terminated by rhombohedra. Cleavage is easy along the faces of the prism. On calcination a mixture of the oxides of zirconium and nickel is left. The percentage of fluorine present was not determined.

2NiF<sub>2</sub>.ZrF<sub>4</sub>.12H<sub>2</sub>O. This salt is easily formed in the presence of an excess of hydrofluoric acid and nickel fluoride. It redissolves in water without change and is not affected by boiling, but on standing flocculent nickel fluoride is deposited. It crystallizes with a deep emerald green color in oblique, rhombic prisms.

KF.NiF<sub>2</sub>.2ZrF<sub>4</sub>.8H<sub>2</sub>O. This is the only triple fluoride reported (468). These crystals are pale green and in the form of oblique, rhombic prisms but with a great many modifications. They are deposited, practically quantitatively, on mixing in equivalent proportions solutions of the double fluorides of potassium-zirconium fluoride and nickel-zirconium fluoride, and are very slightly soluble in water. If the two solutions are in exactly equivalent proportions the mother liquor is entirely decolorized and none of the salts is retained in solution. If the solutions are hot and concentrated a mass of the acicular crystals of the potassium compound is ordinarily deposited and the



mother liquor remains green, but gradually the first crystals are redissolved and the triple compound is formed. The analysis is incomplete as to the fluorine.

There seem to be three types of the double fluorides with the bivalent elements. (1)  $2\text{MF}_2 \cdot \text{ZrF}_4 \cdot 6 \text{ or } 12 \text{ H}_2\text{O}$ ; (2)  $\text{MF}_2 \cdot \text{ZrF}_4 \cdot 6\text{H}_2\text{O}$ ; (3)  $3\text{MF}_2 \cdot 2\text{ZrF}_4 \cdot (\text{H}_2\text{O})_n$ .

In view of the presence of water it is reasonable to assume that all of these are really combinations with zirconyl fluoride and should be written as follows: (1)  $2\text{MF}_2 \cdot \text{ZrOF}_2 \cdot \text{H}_2\text{F}_2 \cdot (\text{H}_2\text{O})_n$ ; (2)  $\text{MF}_2 \cdot \text{ZrOF}_2 \cdot \text{H}_2\text{F}_2 \cdot (\text{H}_2\text{O})_n$ ; (3)  $3\text{MF}_2 \cdot (\text{ZrOF}_2)_2 \cdot \text{H}_2\text{F}_2 \cdot (\text{H}_2\text{O})_n$ . These compounds have not been sufficiently investigated to clear up this question.

The experiments of Piccini (550) with hydrogen peroxide may properly be given here. When titanium fluoride is treated with this reagent the reaction is a reversible one:  $\text{TiF}_4 + \text{H}_2\text{O}_2 \rightleftharpoons \text{TiO}_2\text{F}_2 + \text{H}_2\text{F}_2$ . A solution of potassium fluotitanate ( $2\text{KF} \cdot \text{TiF}_4 \cdot \text{H}_2\text{O}$ ) gives with the peroxide on heating  $2\text{KF} \cdot \text{TiO}_2\text{F}_2$ ; also ammonium fluotitanate gives  $3\text{NH}_4\text{F} \cdot 2\text{TiO}_2\text{F}_2$ . Neither zirconium fluoride nor its double fluorides give this reaction.

*Zirconium-Silicon-Fluoride.* Zirconium hydroxide dissolves slightly in fluosilicic acid. The filtrate becomes cloudy on standing and most of the mass settles out as a jelly. After nearly-completed evaporation of the solution pearly-white crystals, which are easily soluble in water, are formed. The solution clouds on heating (49, 794, 212).

### Zirconium and Chlorine

*Zirconium Tetrachloride ( $\text{ZrCl}_4$ ).* *Preparation.* Zirconium tetrachloride was first prepared by Berzelius (52) by the action of chlorine upon metallic zirconium. The reaction begins on gentle heating and proceeds with incandescence. The presence of water must be carefully guarded against in this as in any method for preparing this salt. It was doubtless due to a failure in this respect that the product obtained by him was a white, non-volatile mass only partially soluble in water. The method is in general unsatisfactory because of the difficulty of procuring pure zirconium. For instance, the metal used by Troost (714) undoubtedly carried some aluminum as well as iron. The tetrachloride was prepared by Wöhler (820), Hermann (319), and Hinzberg (337) by heating a mixture of zirconia and carbon in a

stream of chlorine. Instead of using zirconia Wöhler also used powdered zircon. In trying this method Melliss (480) reported it difficult to separate the silicon tetrachloride—an observation confirmed by Hornberger (356). This difficulty might have been overcome, as Troost and Hautefeuille (718) have shown that silicon tetrachloride undergoes double decomposition when heated with zirconia, yielding silica and zirconium tetrachloride. Troost has also prepared this salt by the action of boron trichloride on zirconia. Smith and Harris (663) found that zirconia reacted with phosphorus pentachloride when heated in a sealed glass tube exhausted of air. The reaction did not begin until the temperature was raised above  $150^{\circ}$  and was complete only after some hours of heating at  $190^{\circ}$ . There was obtained a crystalline mass which was a mixture of the tetrachloride and phosphorus oxychloride. Distilled in a stream of chlorine this gave the nearly-pure tetrachloride in large crystals one-half inch long. Wedekind (785) obtained the chloride when the nitride was heated in a stream of chlorine to a dark red heat, and also (775) by heating zirconium carbide in chlorine. The latter reaction was also noted by Moissan and Lengfeld (501). Chauvenet (120) found that carbonyl chloride at  $400^{\circ}$  reduced zirconia, forming the tetrachloride. When a mixture of carbon monoxide with excess of chlorine is used (749) the reaction is hastened and the initial temperature reduced. Powdered zircon (25) is attacked by carbonyl chloride at  $1250^{\circ}$ – $1300^{\circ}$ . The action of a mixture of chlorine and sulphur chloride was applied by Bourion (95) to zirconia. The reaction was stated to have taken place a little under red heat. The product retains sulphur chloride, which produces a red color that can be removed by reheating in a stream of chlorine. The action of carbon tetrachloride on metallic oxides was noted by Demarcay (174) and, using zirconia, he obtained the tetrachloride at the temperature of boiling sulphur. Camboulives (115) repeated the experiment, noting  $400^{\circ}$  as the temperature at which the zirconia was attacked. Meyer and Wilkens (491) failed to observe any reaction with zirconia at the temperature of the Glaser furnace. The gases formed in the reaction were examined and found to be carbon monoxide, carbon dioxide, carbonyl chloride, and chlorine when using alumina as the metallic oxide. The carbon tetrachloride was introduced by bubbling an inert gas through it. This probably accounts for the failure to get a reaction with zirconia, which is more difficultly attacked. Lely and Hamburger (440) used carbon tetrachloride and chlorine and reported the reaction as taking place at  $800^{\circ}$ .



Venable and Bell (744) found this method the most convenient one for the preparation of the tetrachloride, passing the stream of chlorine through a vessel containing carbon tetrachloride and, thus saturated with its vapor, over the zirconia in a glass tube heated by an electric sleeve. The reaction began at about  $300^{\circ}$  and was abundant at  $550^{\circ}$ – $600^{\circ}$ . The yield is quantitative. They also tried the method, which had been used by Chauvenet and others, dependent upon the dissociation of dried zirconyl chloride. This drying is best done under a stream of hydrochloric acid. The dissociation,  $2\text{ZrOCl}_2 = \text{ZrO}_2 + \text{ZrCl}_4$ , begins at about  $300^{\circ}$  (according to Lely and Hamburger,  $600^{\circ}$ ). The yield in several experiments was less than 10 p.c. of the theoretical, due doubtless to failure in meeting the exact conditions of previous dehydration and subsequent dissociation.

*Properties.* Zirconium tetrachloride is a white, crystalline substance, easily volatilized at about  $300^{\circ}$ , subliming in clear, bright crystals of fair size if care is observed in volatilizing and cooling. The vapor density has been determined at  $440^{\circ}$ – $450^{\circ}$  by Hermann (319) and Deville and Troost (185) with only partially satisfactory results. No modern determinations seem to have been recorded. On exposure to air abundant fumes of hydrochloric acid are given off. The reaction with water is most energetic, evolving much heat and forming zirconyl chloride. Covered with anhydrous hydrofluoric acid and heated zirconium tetrafluoride is formed, Wolter (824). The density of the solid as determined with carbon tetrachloride at room temperature (744) is 2.8. It is reported as dissolving in absolute alcohol with hissing (356, 337), but neither an alcoholate nor hydrate could be obtained from the solution (609). On boiling this solution ethyl chloride was liberated (356). If the alcoholic solution is saturated with hydrogen chloride organic salts of a zirconium tetrachloride-hydrogen chloride of the type  $\text{M}_2\text{H}_2\text{ZrCl}_6$  can be formed where M is pyridin, chinolin, etc. The tetrachloride is also soluble in ether. According to Rosenheim and Hertzmann (611), a molecular compound was formed with the ether but this was not obtained pure. In ethereal solution it can form addition compounds with ammonia and various organic bases. Many compounds are also formed with other organic substances.

*Addition compounds.* With sodium chloride— $2\text{NaCl} \cdot \text{ZrCl}_4$ .—Paykull (536) prepared this compound by heating sodium chloride to fusion in contact with volatilized zirconium tetrachloride.

With potassium chloride. By the same method Weibull (794) prepared a similar compound with potassium chloride.

With ammonia— $\text{ZrCl}_4 \cdot 8\text{NH}_3$ .—Stähler and Denk (674) found that this compound was formed when ammonia was passed for about twelve hours over zirconium tetrachloride at  $16^\circ$  until the weight was constant. Heat is evolved in the reaction and a white powder is left. On heating this ammonia was first lost and then ammonium chloride driven off. The powder is very hygroscopic when exposed to air and loses ammonia. With water it reacts strongly, ammonium chloride being formed and zirconium hydroxide precipitated. Matthews (471) obtained  $\text{ZrCl}_4 \cdot 2\text{NH}_3$  by the same method, passing the stream of ammonia only two hours. When ammonia is passed over the heated tetrachloride (673) a white, unstable compound,  $\text{ZrCl}_4 \cdot 3\text{NH}_3$ , is formed below  $232^\circ$ . Matthews (471) has reported this method as giving  $\text{ZrCl}_4 \cdot \text{NH}_3$  and, on further heating, as losing ammonium chloride and leaving the nitride as final product. He also prepared the compound  $\text{ZrCl}_4 \cdot 8\text{NH}_3$  by passing dry ammonia into a solution of the tetrachloride in absolute ether. Heat was liberated as a white, flocculent precipitate was formed. On drying this salt was found stable in the air. Paykull (536) also prepared  $\text{ZrCl}_4 \cdot 4\text{NH}_3$ .

$\text{NOCl}$ ,  $\text{NO}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{C}_2\text{N}_2$ , and the nitriles give no reaction with zirconium tetrachloride (471, 663). Compounds have been formed (471) by passing vapors of organic amines into an ethereal solution of the tetrachloride.

By saturating absolute alcohol with hydrogen chloride, adding an excess of zirconium hydroxide, and heating with a reflux condenser a solution was obtained by Rosenheim and Frank (609) which was filtered cold and again saturated with hydrogen chloride. This formed well-crystallized salts on the addition of concentrated solutions of pyridin chlorhydrate and quinolinchlorhydrate, with the composition  $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{ZrCl}_6$  and  $(\text{C}_9\text{H}_7\text{N})_2\text{H}_2\text{ZrCl}_6$ , respectively. This solution in absolute alcohol, saturated with hydrogen chloride, therefore contains zirconium tetrachloride, but no hydrate of this was formed (such as had been reported by earlier investigators working under different conditions) nor could any alcoholates be detected.

Organic amines added to aqueous solutions give the same precipitate as ammonia (752, 753).

*Zirconyl Chloride* ( $\text{ZrOCl}_2$ ). This compound is formed by hydrolysis when the tetrachloride is exposed to moist air or dissolved in water. On crystallizing it combines with water of crystallization.



It is also formed by dissolving the hydroxide in hydrochloric acid. From such a solution colorless, needlelike crystals having a somewhat bitter, astringent taste are obtained. If the solution is made strongly acid the crystallization is nearly quantitative, the hydrated zirconyl chloride being only slightly soluble in concentrated hydrochloric acid. The addition of water precipitates this chloride from an acid solution and concentrated hydrochloric acid precipitates it from an aqueous solution. These precipitates are gradually redissolved on standing, this re-resolution depending upon the relative proportions of the precipitant.

These crystals have the composition  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and form tetragonal prisms with distinct cleavage (265, 304). They are stable in air and effloresce over a dehydrating agent, losing hydrochloric acid at the same time. They are easily soluble in water and no precipitate is formed on heating the solution but hydrochloric acid is liberated. They are also soluble in ether and alcohol. Dilute hydrochloric acid dissolves them but the concentrated acid has little solvent action.

The existence of several hydrates of zirconyl chloride has been reported by different investigators. Some of these are manifestly erroneous. The following appear in the literature.  $\text{ZrOCl}_2 \cdot 9\text{H}_2\text{O}$  (319);  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (536);  $\text{ZrOCl}_2 \cdot 6.5\text{H}_2\text{O}$  (537);  $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$  (742);  $\text{ZrOCl}_2 \cdot 5.5\text{H}_2\text{O}$  (434);  $\text{ZrOCl}_2 \cdot 4.5\text{H}_2\text{O}$  (479);  $\text{ZrOCl}_2 \cdot 4\text{H}_2\text{O}$  (434);  $\text{ZrOCl}_2 \cdot 3.5\text{H}_2\text{O}$  (122);  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$  (736);  $\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$  (434, 122). Some of these variations may be accounted for by the conditions under which the investigations were carried out, such as imperfect drying, range of temperature with possible partial hydrolysis, loss of hydrochloric acid, and whether dried in air or in a stream of hydrogen chloride. The hydrates with 9 and with 6.5 molecules of water may be definitely excluded, and quite probably those with 5.5 and 4.5 molecules. Chauvenet (122) from thermochemical data has limited the number to those with 8, 6, 3.5, and 2 molecules of water.

These hydrates have been obtained as follows:

Normally, the zirconyl chloride crystallizes with 8 molecules of water and has the composition  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ . Such crystals are formed whenever the solution is evaporated at ordinary temperature. They are also formed on the addition of concentrated hydrochloric acid to the aqueous solution. If the solution is concentrated a curdy precipitate is formed. The crystals are soluble in boiling hydro-

chloric acid but are deposited again on cooling, and this recrystallization from boiling hydrochloric acid furnishes a method for the purification of the chloride. The crystals of this hydrate may be dried in air without loss of hydrochloric acid. In dry air they effloresce and the loss of water ceases when they reach a weight corresponding to  $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$ . If the dehydration is carried further in a stream of dry air at  $50^\circ$  the limit  $\text{ZrOCl}_2 \cdot 3.5\text{H}_2\text{O}$  is reached (122). If heated in a stream of hydrogen chloride at a temperature not exceeding  $125^\circ$  the composition is  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$  (736). If the temperature is raised to  $150^\circ$   $\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$  is left (122). The last of the water of hydration is lost at  $180^\circ$ – $210^\circ$  (736).

*Hydrolysis of the Chlorides.* As has been stated, zirconium tetrachloride when brought in contact with water is quickly hydrolyzed to zirconyl chloride. This hydrolysis progresses further. Aqueous solutions of zirconyl chloride always have an acid reaction and on standing the salt present undergoes progressive hydrolysis even at ordinary temperature. This hydrolysis is, of course, affected by such conditions as temperature and concentration. Ruer (619) has measured this hydrolysis in a one-fourth normal solution of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  at  $18^\circ$ , according to the time elapsed after solution, by the specific conductivity.

		-5	-1	-1
After 5 minutes	$1469 \times 10$	ohm	c.c.	
" 10 "	1556	"	"	
" 1 hour	1867	"	"	
" 3.5 "	1965	"	"	
" 5 "	1980	"	"	
" 6 "	1989	"	"	
" 24 "	2024	"	"	
" 48 "	2071	"	"	
" 72 "	2104	"	"	
" 168 "	2107	"	"	
" boiling	2777	"	"	
72 hours later	2722	"	"	

This increase in conductivity is due of course to the hydrochloric acid liberated. The change is rapid in the first sixty minutes at an average rate of  $67 \times 10^{-5} \text{ ohm}^{-1} \text{ c.c.}^{-1}$  per minute. For the next 168 hours it is nearly stationary, averaging  $0.014 \times 10^{-5} \text{ ohm}^{-1} \text{ c.c.}^{-1}$  per minute, indicating the formation of a more stable basic chloride which breaks down under the influence of heat with a rapid increase of more than 30 p.c. in conductivity. At this point the liberation of hydrochloric acid seems to come to an end and a slow reversal is shown, doubtless due to the gradual escape of the freed acid or partial



recombination. When ionized in solution the zirconyl radical forms the cation. In a 2 p.c. solution of zirconyl chloride in half-normal hydrochloric acid (time 14 hours, current 0.05 amp.) 0.0280 grams of  $\text{ZrO}_2$  were found in the cathode arm and 0.0005 grams in the anode.

In the course of the hydrolysis and under varying conditions of temperature and concentration certain definite basic zirconyl chlorides are formed. The first of these is  $\text{Zr}_2\text{O}_3\text{Cl}_2$  (on water-free basis) as described by Endemann (209). It may be precipitated from an alcoholic solution of zirconyl chloride by the addition of ether and, as Chauvenet (122) has shown, retains three molecules of water. More properly then the formula may be written  $\text{ZrO}(\text{OH})_2\text{ZrOCl}_2$ . It can be prepared (122) in the water-free condition by heating the hydrate  $\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$  to  $230^\circ$  under hydrogen chloride. This basic chloride is soluble in water and may be transformed into  $\text{ZrOCl}_2$  by adding concentrated hydrochloric acid and warming. At  $300^\circ$  the water-free  $\text{ZrOCl}_2$  and  $\text{Zr}_2\text{O}_3\text{Cl}_2$  dissociate into  $\text{ZrCl}_4$  and  $\text{ZrO}_2$ . Endemann reported also a basic zirconyl chloride with the composition  $\text{Zr}_3\text{O}_4\text{Cl}_2$ , the existence of which has not been confirmed. When zirconyl chloride or the basic chlorides are heated to a high temperature a small portion of the chlorine is retained even after prolonged heating at  $1000^\circ$ . The hydrolysis of zirconyl chloride at  $0^\circ$  and  $20^\circ$  has been measured by Venable and Jackson (749).

In dialyzing zirconyl chloride, Ruer (618) found that a hydrosol with a lower ratio than  $\text{ZrO}_2 : \text{Cl} :: 0.2958 : 0.0060$  was not obtainable. This chlorine could not be separated by silver nitrate except after treatment with nitric acid. A gel of zirconyl hydroxide separated in the dialysis. The hydrosol contained colloidal hydroxide which could be freed from the small amount of chlorine by adding first silver nitrate in the proper amount, then nitric acid, and warming or agitating. By evaporating a dilute solution of zirconyl chloride to a very small volume, diluting and evaporating again three or four times, most of the hydrochloric acid liberated on hydrolysis was driven off, Ruer (619). The liquid became opalescent and finally milky. The final evaporation left about 15 c.c. A very finely divided precipitate settled out, leaving a liquid in which very little zirconium could be detected. Washing with water caused the liquid to become milky once more. The precipitate was centrifuged. Concentrated hydrochloric acid was added and the centrifuging repeated. Water was added, then hydrochloric acid, and the mixture centrifuged, and these operations repeated. The yield of precipitate was almost quantitative. It was

dried in vacuo over sulphuric acid and over potassium hydroxide and yielded a loose white powder. Four preparations showed this to be of practically constant composition. No formula for the substance is given by Ruer, but on calculation from his analyses its composition corresponds closely with  $9\text{ZrO}(\text{OH})_2 \cdot \text{ZrOCl}_2 \cdot \text{aq}$ . It was only partially dried when heated to  $130^\circ$ , losing almost no hydrochloric acid, showing that part of the water is very firmly held. This compound Ruer (619) called metazirconic chloride. It is really a highly hydrolyzed basic chloride and on the water-free basis might be represented by the formula  $\text{Zr}_{10}\text{O}_{19}\text{Cl}_2$ . The formula given above goes to show that out of 10 molecules of zirconyl chloride 9 had undergone hydrolysis. This substance before drying is soluble in water. On dialyzing this solution a colloidal solution containing less than 1 p.c. of chlorine is obtained; hence it is a solution of nearly pure zirconyl hydroxide or metazirconic acid. It is difficult to transform this basic chloride into zirconyl chloride by the action of hydrochloric acid after once removing the excess of water. After boiling five grams with a half-liter of concentrated hydrochloric acid for three hours only 20 p.c. had been changed. For complete change it was necessary to heat it with one kilo for thirty hours.

By dissolving zirconium hydroxide in hydrochloric acid, concentrating, and crystallizing it has been claimed (247) that a crystalline mixture of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Zr}_5\text{O}_8\text{Cl}_2 \cdot 22\text{H}_2\text{O}$  is obtained. It is stated that this new basic chloride can be separated from hydrochloric acid by recrystallization. The existence of this salt with its peculiar behavior lacks confirmation. The existence of a basic chloride  $\text{Zr}_4\text{O}_2\text{Cl}_6$ , which Troost and Hautefeuille (716) reported as formed when  $\text{ZrCl}_4$  was heated in a stream of oxygen, has been shown by Chauvenet (122) to be an error. If the oxygen is not thoroughly dried a small amount of the tetrachloride is hydrolyzed to zirconyl chloride, which breaks up on heating into zirconia and chlorine. This zirconia in small amounts may be entrained in the vapor of the tetrachloride. In larger amounts its presence is shown by its insolubility.

*Double compounds.* Nilson (518) on mixing a solution of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  with chloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ , obtained crystals in the form of small, clear, yellow prisms. They were fairly stable in the air. The melting point was  $100^\circ$ . One-half the water was lost at this temperature, giving a shellac-like mass. The composition is represented by the formula  $\text{ZrOCl}_2 \cdot \text{PtCl}_4 \cdot 12\text{H}_2\text{O}$ . Also a compound



was obtained with platinous chloride which had the composition  $\text{ZrOCl}_2 \cdot \text{PtCl}_2 \cdot 8\text{H}_2\text{O}$ .

*Compounds with Chloric Acid.* The normal chlorate  $(\text{ZrClO}_3)_4$  has probably not been prepared, though Weibull (794) stated that he had prepared it by double decomposition according to the equation  $\text{Zr}(\text{SO}_4)_2 + 2\text{Ba}(\text{ClO}_3)_2 = \text{Zr}(\text{ClO}_3)_4 + 2\text{BaSO}_4$ . No details or analyses are given. This is manifestly erroneous, since both zirconium sulphate and chlorate are hydrolyzed in aqueous solution. A basic zirconyl chlorate has been prepared by Venable and Smithey (751) by adding a solution of potassium chlorate to a cold solution of zirconium perchlorate, crystallizing out the potassium perchlorate, and allowing the basic zirconyl chlorate to crystallize over phosphorus pentoxide. It forms fairly large, distinct crystals which were very deliquescent and could not be dried over sulphuric acid or calcium chloride. They were soluble in alcohol but not in ether. These crystals oxidize organic matter and are slightly yellowish in color from partial decomposition, chloric acid being liberated with the formation of chlorine dioxide. The composition of the crystals agrees with the formula  $\text{ZrO}(\text{OH})_2 \cdot 3\text{ZrO}(\text{ClO}_3)_2$ .

*Compounds with Perchloric Acid.* The normal zirconyl perchlorate has not been prepared. An acid perchlorate or zirconyl perchloric acid has, however, been prepared by Venable and Smithey (751) by dissolving the hydroxide in perchloric acid at ordinary temperature in the presence of an excess of hydroxide. It forms large crystals of the triclinic system, which explode when sharply heated. The analyses correspond with the formula  $4\text{ZrO}(\text{ClO}_4)_2 \cdot \text{ClO}_4\text{H}$ .

When the perchloric acid was saturated with zirconyl hydroxide by heating on a water bath with excess of hydroxide radiating clusters of crystals were formed from which single crystals could not well be separated. These were very deliquescent, soluble in alcohol, ether, benzene, chloroform, and carbon tetrachloride, but no crystals were obtained from these solutions. A small portion, heated rapidly on platinum, exploded with a sharp report. Decomposition was evident at  $100^\circ$ . Slowly heated they intumesced and finally left a white powder of zirconia. Several preparations were made. The analyses correspond with the formula  $\text{ZrO}(\text{OH})_2 \cdot 9\text{ZrO}(\text{ClO}_4)_2$ . One molecule of the zirconyl perchloric acid therefore seems to dissolve one molecule of zirconyl hydroxide, giving a compound in which the ratio of zirconyl hydroxide to zirconyl perchlorate is 1 : 9. On recrystallizing

this product it is dissociated and the original zirconyl perchloric acid formed (751).

### Zirconium and Bromine

*Zirconium Tetrabromide* ( $\text{ZrBr}_4$ ). This has been prepared (480) by passing carbon dioxide saturated with bromine vapors over a mixture of zirconia and charcoal heated to a bright red heat. It forms a white, crystalline powder which can be volatilized without decomposition. It is not reduced by hydrogen at a white heat but is decomposed by moist air and reacts energetically with water, yielding a solution of zirconyl bromide. It has also been prepared by passing bromine vapors over heated zirconium (22) or the carbide (674). Here, also, a stream of carbon dioxide may be used as the carrier. It is very hygroscopic, giving off hydrobromic acid. It is soluble in alcohol or ether.

The tetrabromide forms compounds with ammonia in a manner similar to the tetrachloride. Thus, when saturated with ammonia passing over it at  $16^\circ$  it forms the compound  $\text{ZrBr}_4 \cdot 10\text{NH}_3$  (674). This is a very hygroscopic white powder, giving off ammonia. If warmed (472) it forms a somewhat more stable compound  $\text{ZrBr}_4 \cdot 4\text{NH}_3$ , which on heating gives the nitride and by further heating in hydrogen yields the metal. With ethylamine the compound  $\text{ZrBr}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$  is formed; with anilin,  $\text{ZrBr}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ ; and with pyridin  $\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ , showing the same power of forming addition compounds with organic bases that the tetrachloride has. Rosenheim and Frank (609), by the addition of pyridin and chinolin to a solution of hydrogen bromide in alcohol saturated with zirconium hydroxide, obtained the compounds  $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{ZrBr}_6$  and  $(\text{C}_9\text{H}_7\text{N})_2\text{H}_2\text{ZrBr}_6$ .

*Zirconyl Bromide* ( $\text{ZrOBr}_2$ ). This can be prepared by dissolving zirconyl hydroxide in hydrobromic acid and allowing the solution to evaporate to crystallization. It can also be prepared by the hydrolysis of the tetrabromide in aqueous solution or by dissolving the hydroxide in a saturated solution of hydrogen bromide in absolute alcohol. The crystals are granular (44) or fine, brilliant, needlelike (742), optically uniaxial, tetragonal, and isomorphous with the corresponding zirconyl chloride. The formula usually assigned them is  $\text{ZrOBr}_2 \cdot 8\text{H}_2\text{O}$ , but it is difficult to remove the surplus water without decomposition, so as much as 13 and 14 molecules of water of crystallization have been reported. The crystals readily lose hydrobromic acid in a current of dry air or when placed over a dehydrating agent.



They are more hygroscopic than the zirconyl chloride crystals, decomposing on exposure to moist air. These crystals are soluble in hot, concentrated hydrobromic acid, crystallizing out again on cooling. Dried at  $100^{\circ}$ – $120^{\circ}$  in a rapid stream of hydrogen bromide a hard, crystalline solid (742) which is readily soluble in water is obtained. This has the composition  $\text{ZrOBr}_2 \cdot 4\text{H}_2\text{O}$ .

*Basic Zirconyl Bromide*  $\text{ZrO}(\text{OH})_2 \cdot \text{ZrOBr}_2 \cdot 3\text{H}_2\text{O}$  (or  $4\text{H}_2\text{O}$ ). This basic salt (742) was obtained by the prolonged boiling of a saturated solution of the hydroxide in concentrated hydrobromic acid and subsequent evaporation of the solution (deeply colored with bromine) on a water bath. White crystals with the composition  $\text{ZrO}(\text{OH})_2 \cdot \text{ZrOBr}_2 \cdot 4\text{H}_2\text{O}$  separated out. Gelatinous zirconyl hydroxide was also distributed through the solution. Another crop of smaller needlelike crystals was obtained on further evaporation of the solution. These had the composition  $\text{ZrO}(\text{OH})_2 \cdot \text{ZrOBr}_2 \cdot 3\text{H}_2\text{O}$ . The gelatinous hydroxide, retaining some bromine, could be separated as a hydrogel by dialysis, the basic zirconyl bromide going into solution. A basic zirconyl bromide of a similar composition was obtained also by Weibull (795).

### Zirconium and Iodine

*Zirconium Tetraiodide* ( $\text{ZrI}_4$ ). Attempts to prepare this salt by the action of iodine upon a mixture of zirconia and carbon raised to a high temperature have failed (480). Nor was it formed when vapors of the tetrabromide were passed over heated potassium iodide (480.) Furthermore, iodine seems to have slight direct action upon metallic zirconium (22, 480). Hydrogen iodide, however, acts upon the metal at  $340^{\circ}$  or upon the carbide at  $490^{\circ}$ . The reaction is energetic and a rust-brown sublimate is formed intermixed with iodine crystals. No white sublimate was observed by Stähler and Denk (673). The excess of iodine was removed by washing with benzene, leaving a red-brown residue which appeared as a crystalline powder when examined under the microscope. This fumed in the air and dissolved in water with energetic reaction. It also reacted energetically with alcohol, giving zirconyl hydroxide and ethyl iodide. It is slightly soluble in benzene or carbon disulphide and more readily soluble in ether, giving a yellow addition product. It is strongly hydrolyzed by water and decomposed by strong acids (673). Older statements that are apparently irreconcilable with these occur in the literature (176).

The possible existence of a periodide,  $\text{ZrI}_4 \cdot \text{I}_2$ , has been based (674) upon the fairly constant proportions observed in the product obtained in the preparation of the tetraiodide before the treatment with benzene. On subliming this product at a temperature over  $300^\circ$  a heavy, dark-brown vapor, which condensed to a red-brown powder, was formed.

*Addition compounds.* Addition compounds are formed by the tetraiodide with ammonia. When a stream of dry ammonia is passed (674) over crystals of the tetraiodide at a temperature not exceeding  $22^\circ$  a constant weight is reached at which the composition corresponds to the formula  $\text{ZrI}_4 \cdot 8\text{NH}_3$ . This substance, according to Stähler and Denk, may be regarded possibly as a double compound of the amid and ammonium iodide, and on that basis would be ascribed the formula  $\text{Zr}(\text{NH}_2)_4 \cdot 4\text{NH}_4\text{I}$ . Liquid ammonia largely dissolves and separates the ammonium iodide. Against this view, however, may be considered the gradual loss of ammonia on raising the temperature. At  $100^\circ$  the composition is  $\text{ZrI}_4 \cdot 7\text{NH}_3$ ; at  $150^\circ$  it is  $\text{ZrI}_4 \cdot 6\text{NH}_3$ ; and up to  $200^\circ$  it is  $\text{ZrI}_4 \cdot 4\text{NH}_3$ . At this temperature decomposition begins to take place and ammonium iodide is driven off. Supposedly it follows the analogy of the corresponding chlorine and bromine compounds, and at temperatures over  $300^\circ$  is changed to the nitride which may be reduced by heating with hydrogen. The probable formation of addition compounds with organic bases has not been investigated. Stähler and Denk (674) have prepared a compound with ether which has the composition  $\text{ZrI}_4 \cdot 4(\text{C}_2\text{H}_5)_2\text{O}$ .

*Zirconyl Iodide.* The normal salt,  $\text{ZrOI}_2$ , has been prepared by the hydrolysis of the tetraiodide (674). It crystallizes in colorless needles having the composition  $\text{ZrOI}_2 \cdot 8\text{H}_2\text{O}$ . These are very hygroscopic and are soluble in water or alcohol. The preparation of this salt by dissolving the hydroxide in hydriodic acid presents several difficulties (742). Zirconyl hydroxide is scarcely attacked by this acid; hence the cold precipitated zirconium hydroxide must be used. Even this is only sparingly dissolved. The best results are obtained when hydrogen iodide is passed into water in which the hydroxide is suspended. The evaporation to the crystallizing point brings about decomposition of the hydriodic acid and the crystals formed are colored with iodine, which is difficult to remove by treatment with benzene or carbon disulphide. The hydrolysis proceeding during these operations brings about the formation of basic salts.

*Basic Zirconyl Iodides.* The compound  $\text{ZrO}(\text{OH})_2\text{ZrOI}_2 \cdot 5\text{H}_2\text{O}$



has been prepared by Hinsberg (337) by the double decomposition of barium iodide with zirconyl sulphate in solution. It is an amorphous, colorless powder which decomposes in the air, becoming colored with iodine. It is soluble in water. A still more basic substance was obtained by Venable and Baskerville (742) by the action of hydriodic acid upon zirconium hydroxide suspended in water and the evaporation of the solution. To limit the decomposition and separation of iodine this evaporation may be carried out in an atmosphere of carbon dioxide, in which case the salt  $\text{ZrOI}_2 \cdot 8\text{H}_2\text{O}$  is obtained (674). Ordinary evaporation gave a hard, hornlike, colored mass.

*Zirconyl Iodate.* The normal salt,  $\text{ZrIO}_3$ , has not been prepared. Basic iodates are formed (751) when a solution of iodic acid is added to a solution of zirconyl chloride. The white precipitate is quite insoluble in water or dilute nitric acid; hence the precipitation is practically complete, and this has been recommended as a means of separation for zirconium analytically. A series of basic zirconyl iodates are formed according to the concentration of the solutions used, the temperature, and the extent of the washing of the precipitate.

*Zirconyl Periodate.* This substance has been prepared by Weibull (794) as a white precipitate, insoluble in water, by adding a solution of periodic acid to one of zirconyl chloride. No details are given as to composition.

## Chapter V

### Compounds with the Acids of Sulphur and Selenium

#### Compounds Formed with Sulphurous Acid

*Zirconium Sulphite*  $\text{Zr}(\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$ . This has been prepared (740) by suspending the hydroxide in water and saturating with sulphur dioxide, separating the insoluble basic salts formed, and allowing the solution to evaporate to less than one-twentieth of its bulk over sulphuric acid. Hard, white, warty crystals attached themselves firmly to the sides of the dish. The analysis showed their composition to correspond with the above formula.

*Basic Zirconyl Sulphites*. Several basic salts have been reported. Hermann (320) found that ammonium sulphite gave a basic precipitate when added to a solution of a zirconium salt. This was soluble in an excess of the ammonium sulphite. Zirconium hydroxide was not precipitated from this solution by alkalis while cold, but a precipitate formed on boiling. The formation of a precipitate on passing sulphur dioxide into a solution of a zirconyl salt was also observed by Berthier (43). This precipitate is not readily formed if zirconyl sulphate is used, even after boiling (740). It forms readily when a nearly neutral solution of zirconyl chloride is used, especially after boiling. This precipitate varies in composition, the ratios of zirconia to sulphur dioxide in several preparations ranging from 2 : 1 to 4 : 1, showing an excess of base.

The precipitation of zirconium by means of sulphur dioxide is not, under ordinary conditions, complete nor does it bring about a complete separation from iron, for which purpose it has been recommended, but for many purposes the degree of elimination of iron is satisfactory.

*Zirconyl Thiosulphate*. Sodium thiosulphate forms a precipitate when added to a neutral solution of the chloride (686). A partial investigation of this (740) showed that the precipitate varied in composition according to the extent of hydrolysis and consisted of basic forms of zirconyl thiosulphate.



### Compounds with Sulphuric Acid

*Normal Zirconium Sulphate* ( $\text{Zr}(\text{SO}_4)_2$ ). This salt was first prepared by Berzelius (53) by heating zirconia with an excess of concentrated sulphuric acid and driving off the excess of sulphuric acid below a red heat. He reported it as stable up to a low red heat but stated that it decomposed at higher temperatures, also that it crystallized from  $\text{H}_2\text{SO}_4$  but better from water. Undoubtedly a red heat is too high, and some of the combined acid was driven off. Other investigators (22, 293, 795) have shown that lower temperatures must be used for driving off the excess of acid, the range being  $350^\circ$ – $400^\circ$ . Hauser (293) prepared the sulphate by treating incompletely dried zirconia, which dissolves more readily, with concentrated acid and then driving off the excess acid at  $360^\circ$ – $380^\circ$ . This may be done conveniently in a Kjeldahl flask over which is fitted a small funnel connected with a suction pump for carrying off the fumes and preventing the access of dust. Dried zirconia is acted upon slowly and with difficulty, and ignited zirconia is scarcely attacked at all. The salt is quite stable and only traces of the combined acid are lost after heating at  $380^\circ$  for eight to ten hours. If a gas burner is used for the heating the product must be protected from the water formed in the combustion of the gas, as this partially hydrolyzes the sulphate.

The neutral water-free sulphate dissolves slowly in water, evolving a considerable amount of heat. This Hauser (293) attributed to the formation of the tetrahydrate,  $\text{Zr}(\text{SO}_4)_2 + 4\text{H}_2\text{O} = \text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , which then dissolves without heat evolution but is hydrolyzed to zirconyl sulphate. The heat of formation from the action of sulphuric acid upon the hydroxide is given by Pissarjewski (554) as 11,670 cal. The tetrahydrate  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  forms rhombic or small tabular crystals. It is insoluble in alcohol. Three molecules of water are lost on heating at  $100^\circ$ – $120^\circ$ , the fourth only on prolonged heating at a higher temperature short of decomposition (536, 610). On slow concentration of a solution of zirconium sulphate containing an excess of sulphuric acid a crystalline crust is formed. This retains water of crystallization. When an aqueous solution to which no acid has been added is evaporated the hydrolysis is far-reaching and a gumlike mass is left. Sulphur trioxide is driven off on ignition of the sulphate, but heating for some time at a temperature of  $900^\circ$ – $1000^\circ$  fails to remove the last traces. Bailey (22) heated it with ammonium carbonate in order to remove the last of the sulphur tri-

oxide but according to other investigators this involved the loss of some zirconia. The anhydrid  $2\text{ZrO} \cdot \text{SO}_3$  is left when the sulphate is heated for some time at  $200^\circ$ – $300^\circ$  in the presence of water vapor. This is commonly found in commercial preparations of the sulphate.

The normal zirconium sulphate is readily hydrolyzed when dissolved in water, giving a strong acid reaction. The extent of this hydrolysis depends upon the extent of the dilution, the time elapsed, and the temperature. For instance, the specific conductivity of a 1.75 p.c. solution at  $18^\circ$  when determined immediately after preparation was found by Ruer and Levin (621) to be  $3105 \times 10^{-5} \text{ ohm} \times \text{c.c.}^{-1}$ . After twenty hours it was 3186; after boiling 3418. Twenty-four hours later it was 3432 and this had not changed after standing seventy-two hours. Very dilute solutions become opalescent on boiling and the hydroxide separates. These become clear again on concentration. The work of Venable and Jackson (750) would indicate that on dissolving the normal sulphate  $\text{Zr}(\text{SO}_4)_2$  at  $0^\circ$  and also at  $20^\circ$  there was for the first three observations taken at 5-minute intervals a slight increase of resistance followed by a slow decrease for three hours. After that an equilibrium was reached. The behavior in the first 15 minutes was doubtless due to change in reaching a temperature equilibrium. The addition of alcohol to solutions of the normal sulphate causes the precipitation of basic zirconyl salts. Crystalline basic salts also form under certain conditions of dilution and temperature (295) and the boiling of dilute solutions gives precipitates of basic compounds (601).

*Acid Sulphates or Zircon-Sulphuric Acid.* The existence of such compounds for the normal sulphate has been questioned but seems probable. The subject was brought under investigation by the difference shown by the sulphate from certain other zirconium salts in its behavior towards various reagents, such as oxalic acid or ammonium oxalate. This has been studied by a number of investigators and several theories have been formulated as to the constitution of the sulphate when dissolved. Hauser (296) found that the solubility of the sulphate in  $\text{H}_2\text{SO}_4$  decreased with the increase of concentration of the acid up to a certain point and then suddenly and notably increased to a point at which a slightly increased concentration decreased the rate of solution. By using a concentration greater than 61.4 p.c. there may be obtained a clear liquid which, on standing a number of days, deposits fine, monoclinic, needlelike crystals quite different in form from those of the salt  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . The analysis cor-



responded to the composition  $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ . The formation of these crystals is easy to overlook as they crystallize slowly. The exact conditions for their formation are as follows: The tetrahydrate,  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , is practically insoluble in water containing 45-55 p.c. of  $\text{SO}_3$ ; with more than 57 p.c. there is a rapid increase in solubility. The reaction, as stated by Hauser,  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \rightleftharpoons \text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , takes place at  $39.5^\circ$  and a concentration of 61.4 p.c.  $\text{SO}_3$ . On melting this trihydrate with much concentrated  $\text{H}_2\text{SO}_4$  in a glass tube and allowing it to stand for some days a compact, crystalline powder, which on analysis gave the monohydrate  $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , is formed. These hydrates Hauser called hydrates of zircon-sulphuric acid,  $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4$ . He also noted that the boiling points of solutions of  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in concentrated  $\text{H}_2\text{SO}_4$  slowly but materially fall on heating, and basic zirconyl salts separate as crystals or precipitates. In the electrolysis of this zircon-sulphuric acid the zirconium formed a complex anion. Thus  $\text{H}_2[\text{Zr}(\text{SO}_4)]_3 \rightleftharpoons 2\text{H}^+, \text{Zr}(\bar{\text{S}}\bar{\text{O}}_4)_3$ . The behavior under electrolysis would manifestly depend largely upon the dilution, and the presence of water brings about hydrolysis. It is quite possible, therefore, for the solid salt to be zirconium bisulphate. Double salts have been obtained with the alkaline sulphates.

Ruer (617) in his investigation of the constitution of zirconium sulphate tetrahydrate reached the conclusion that in aqueous solution the formula should be  $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4$ , which undergoes a progressive further hydrolysis unless excess of acid is present. Further, he contended that in the crystalline form the constitution is to be expressed by the formula  $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ . He found the electrical dissociation in solution to be  $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+, \text{ZrO}(\bar{\text{S}}\bar{\text{O}}_4)_2$ , the zirconium migrating with the negative stream. Double salts with sodium, as  $\text{Na}_2\text{SO}_4 \cdot \text{ZrOSO}_4$ , dissociate in the same way. It has been shown also that the supposed  $\text{ZrSO}_4 \cdot 4\text{H}_2\text{O}$  loses three molecules of water at  $100^\circ$ , the fourth molecule being lost only after prolonged heating at a higher temperature, indicating the absorption of energy in the dissociation of the molecule and re-formation of water. Chauvenet and Gueylard (134) found that cryoscopic measurements gave the molecular weight of the sulphate in solution as 79.4 instead of 286.6, or approximately four independent particles to the molecule. Analysis gave the probable form as  $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4$ . Conductivity

experiments during neutralization with NaOH indicated the presence of three compounds,  $\text{ZrOSO}_4$ ,  $\text{ZrOSO}_4 \cdot \text{ZrO}_2$ , and  $3\text{ZrOSO}_4 \cdot \text{ZrO}_2$ .

The addition of alcohol to the solution of the sulphate gives basic precipitates. The objection may be raised here that the alcohol itself has a hydrolyzing effect. The use of ether, which is not open to this objection, also yields strongly basic compounds. Rosenheim and Frank (609) assumed, on the basis of their experiments, the existence of an equilibrium  $2\text{ZrO}(\text{SO}_4\text{H})_2 + \text{H}_2\text{O} \rightleftharpoons \text{Zr}_2\text{O}_3(\text{SO}_4\text{H})_2 + 2\text{H}_2\text{SO}_4$ . Other work bearing on this subject may be found in references 568, 570, 38, 561.

The mass of evidence would go to show that zirconium sulphate,  $\text{Zr}(\text{SO}_4)_2$ , exists only in the entire absence of water. The normal sulphate dissolves slowly in water. Attempts at making a one-fifth molar solution at  $0^\circ$  left a portion undissolved, but the one-tenth molar was made, evolving considerable heat and requiring some 15 minutes for temperature adjustment (750). The hydrolysis then progresses, reaching apparently an equilibrium after 3-4 hours, or at least a point at which the velocity of reaction is very slight. The velocity also diminishes with decreasing temperature. Basic salts may settle out and these will be described under that heading (296). The normal sulphate crystallizes from concentrated  $\text{H}_2\text{SO}_4$  without change. With a concentration of 50-60 p.c.  $\text{SO}_3$  the bisulphate crystallizes. Below that concentration zirconyl acid sulphate,  $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , is obtained in crystalline form. With still greater dilution crystalline basic zirconyl salts are formed.

*Double Salts of Zirconium Sulphate with the Alkaline Sulphates.* Rosenheim and Pinkske (612) have reported that normally constituted double alkali sulphates separate from a solution of  $\text{Zr}(\text{SO}_4)_2$  in  $\text{H}_2\text{SO}_4$  on the addition of solutions of the alkali sulphates. These are regarded as derivatives of  $\text{H}_4(\text{Zr}(\text{SO}_4)_4)$ . They may also be looked upon as double salts with zirconium bisulphate,  $\text{K}_2\text{SO}_4 \cdot \text{ZrH}_2(\text{SO}_4)_3$ . They undergo hydrolysis in water.

The normal double sulphate,  $2\text{K}_2\text{SO}_4 \cdot \text{Zr}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , which may be written as the potassium salt of the above complex acid, is formed when potassium bisulphate in concentrated solution and at boiling temperature is saturated with  $\text{Zr}(\text{OH})_4$ , freshly precipitated in the cold (609, 610). The salt forms in very soluble, needlelike crystals. Analogous salts of sodium and ammonium have also been formed. When  $\text{KHSO}_4$  is added to a solution of  $\text{Zr}(\text{SO}_4)_2$  basic zirconyl sulphates form.



*Zirconyl Sulphate.* Berzelius (53), by saturating a solution of zirconium sulphate with the hydroxide and evaporating, obtained a gumlike mass which became white on drying. On further heating it intumescend and lost water. On ignition it lost additional water and  $\text{SO}_3$ . The analysis gave the ratio  $\text{ZrO}_2 : \text{SO}_3 :: 100 : 65.9$ . The original gum could be dissolved in a small amount of water but gave a precipitate on the further addition of water. From a similar solution by neutralizing with ammonia Kulka (417) prepared a gelatinous substance having the same composition. The gummy mass separated out and was soluble in water but insoluble in acid. According to the view of Hauser (292), these were to be regarded as solutions of the colloidal hydroxide in the neutral sulphate. He found that fresh cold-precipitated hydroxide, which is largely  $\text{Zr}(\text{OH})_4$ , dissolved more easily. Concentrated solutions of the sulphate digested at  $60^\circ$  with this hydroxide for several days gave a solution containing  $\text{ZrO}_2 : \text{SO}_3 :: 1.15 : 1$ . Other investigators have reported this ratio as 1 : 1. Much less of the hot-precipitated hydroxide is dissolved. Zirconyl sulphate was not obtained on evaporating this solution.

Though zirconyl sulphate  $\text{ZrOSO}_4$  is doubtless the first stage in the hydrolysis of the sulphate, it seems to be quickly converted into basic salts and no account of its separation has been given that is not open to criticism. As has been already shown, the crystalline tetrahydrate  $\text{ZrSO}_4 \cdot 2 \cdot 4\text{H}_2\text{O}$  should have assigned to it the formula  $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , and hence may be regarded as the hydrate of a zirconyl sulphuric acid or of the acid zirconyl sulphate whose formula would be  $\text{ZrO} \begin{array}{c} \text{H} \backslash \\ \text{SO}_4 \\ \text{H} / \end{array} \text{SO}_4$ . This corresponds to zircon-sulphuric acid

or acid zirconium sulphate  $\begin{array}{c} \text{H} > \text{SO}_4 \\ \text{Zr} = \text{SO}_4 \\ \text{H} > \text{SO}_4 \end{array}$ .

Zirconyl sulphate is reported by Chauvenet (130) as water-free  $\text{ZrOSO}_4$  and in the following hydrates:  $\text{ZrOSO}_4 \cdot 4\text{H}_2\text{O}$ ;  $\text{ZrOSO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{ZrOSO}_4 \cdot \text{H}_2\text{O}$ . The acid sulphate is given as  $\text{ZrOSO}_4 \cdot \text{SO}_3$ ;  $\text{ZrOSO}_4 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ ;  $\text{ZrOSO}_4 \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$ .

*Basic Zirconyl Sulphates.* The boiling points of solutions of  $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  in  $\text{H}_2\text{SO}_4$  decrease slowly but materially on prolonged heating. This, according to Hauser (296), is to be referred

to the formation of a basic salt,  $2\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 5\text{H}_2\text{O}$ , which separates in crystalline form from very concentrated solutions. Less concentrated solutions give a flocculent precipitate on boiling. This deposition of crystals causes a fall in temperature. At a definite dilution the basic salt,  $4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 14\text{H}_2\text{O}$ , separates, the extent of dilution necessary depending upon the temperature. With increase of temperature a greater dilution becomes necessary and on very great dilution no precipitation is observed. The velocity of the reaction is slight and diminishes with decreasing temperature so that the solution may require prolonged standing for the detection of the deposit. It is best observed at a temperature of  $39.5^\circ$ . As reported by Hauser, the solution remained clear for dilutions  $\text{Zr}(\text{SO}_4)_2 : \text{H}_2\text{O} :: 3 : 8.3 :: 3 : 10 :: 3 : 16$ , but precipitation began at  $3 : 20$  and continued up to a dilution of  $1 : 120$  after standing for ten hours at  $39.5^\circ$ . The crystalline salt,  $4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 14\text{H}_2\text{O}$ , was therefore not decomposed at that temperature and dilution. Its solubility is less than 0.009 p.c. It was found that the original salt had been hydrolyzed in this way to the extent of 66-67 p.c. of the total. Dilute  $\text{H}_2\text{SO}_4$  dissolves this salt very slowly, concentrated acid readily. The element of time in this change is important, and ranges for dilute solutions from two to five days. From these observations it will be seen that the nature of a solution of zirconyl sulphate depends largely upon its previous history. It may be noted that the formula for this basic salt may also be written  $\text{ZrO}(\text{OH})_2 \cdot 3\text{ZrOSO}_4 \cdot 13\text{H}_2\text{O}$  in agreement with the analysis and also with the fact that very dilute solutions are opalescent and yield the colloidal hydroxide  $\text{ZrO}(\text{OH})_2$  on being dialyzed. Very dilute solutions of this basic sulphate which have been heated for a time at  $64^\circ$  have lost the power of forming the crystalline deposit when allowed to stand at a lower temperature. They also show analytical differences. No immediate precipitate is given with  $\text{H}_2\text{O}_2$  but only after standing. Oxalic acid in small amount also gives none. The formation of this indifferent stage seemed to depend in large measure upon the concentration. Concentrated solutions after being heated and then diluted behaved differently from those which were first diluted and then heated (296).

A basic salt,  $2\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 5\text{H}_2\text{O}$ , crystallized from very concentrated solutions and a flocculent precipitate, doubtless without definite composition, separated from quite dilute solutions. This latter is very slightly soluble in water, giving a weakly acid reaction. It is slowly dissolved in dilute  $\text{H}_2\text{SO}_4$  but rapidly dissolved when the



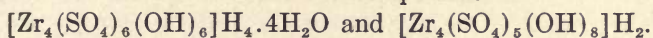
acid has a 30 p.c. concentration. On drying at  $300^{\circ}$  the composition was  $2\text{ZrO}_2 \cdot 3\text{SO}_3$ , Hauser (293).

According to Berzelius (53), a flocculent basic substance with the composition  $3\text{ZrO}_2 \cdot 2\text{SO}_3$  is formed when alcohol is added to a solution of the sulphate. Paykull (536) prepared a substance having a similar composition as a fine-grained precipitate by considerably diluting the solution and washing the precipitate with boiling water. This was insoluble in water and soluble in hydrochloric acid, and was hydrated. The formula was calculated on the dry basis. Endemann (209) using alcohol as a precipitant and very concentrated aqueous solutions of the sulphate, prepared a basic substance having the composition  $7\text{ZrO}_2 \cdot 6\text{SO}_3 \cdot 14\text{H}_2\text{O}$ , which retained some of the alcohol. The addition of very little water freed the alcohol; more cold water dissolved the precipitate; and on driving off the water an amorphous mass was left. If much water was used in dissolving an insoluble basic salt separated. There is little evidence that these compounds were not mere mixtures.

Chauvenet (128, 130), by determining the densities in nitrobenzene at  $12.4^{\circ}$ , obtained a curve with composition and density as the coordinates. This gave six points of inflection corresponding to the basic salts  $\text{Zr}(\text{SO}_4)_2$ ;  $\text{Zr}(\text{SO}_4)_2 \cdot \text{ZrO}_2$ ;  $5\text{Zr}(\text{SO}_4)_2 \cdot 7\text{ZrO}_2$ ;  $3\text{Zr}(\text{SO}_4)_2 \cdot 5\text{ZrO}_2$ ;  $\text{Zr}(\text{SO}_4)_2 \cdot 3\text{ZrO}_2$ ; and  $\text{Zr}(\text{SO}_4)_2 \cdot 2\text{ZrO}_2$ .

Patents have been issued for methods of preparation of a basic sulphate  $5\text{ZrO}_2 \cdot 2\text{SO}_3 \cdot 14\text{H}_2\text{O}$  (608) and also one having the composition  $5\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 13\text{H}_2\text{O}$ .

Hauser and Herzfeld (300) have ascribed the following hypothetical formulas to the basic sulphates obtained by them. One compound crystallized in needles having parallel extinction. The composition was  $\text{Zr}_4(\text{SO}_4)_3(\text{OH})_{10} \cdot 10\text{H}_2\text{O}$ . Another compound obtained in spheroidal crystals had the formula  $[\text{Zr}_4(\text{SO}_4)_2(\text{OH})_{11}]_2 \cdot \text{SO}_4 \cdot 8\text{H}_2\text{O}$  assigned to it. Also there were the compounds



The only double compound prepared in a pure form was obtained by dissolving  $\text{Zr}(\text{SO}_4)_2 \cdot 10\text{H}_2\text{O}$  in 15 c.c. of water, adding 1 c.c. of concentrated  $\text{H}_2\text{SO}_4$ , and then adding dropwise, without stirring, a concentrated solution of  $\text{K}_2\text{SO}_4$  until the original precipitate almost disappeared, leaving a cloudy liquid. The formula assigned the crystalline deposit was  $\text{K}_2\text{Zr}_4(\text{SO}_4)_5(\text{OH})_8$ .

*Double Salts of Zirconyl Sulphate with the Alkali Sulphates.* When potassium sulphate, either in crystals or in saturated solution,

is added in excess to a solution of zirconyl sulphate all of the zirconium is gradually precipitated as a crystalline double salt of varying composition. The excess of the potassium sulphate remaining in the solution is changed partly into the bisulphate. The composition of the basic double salt depends upon the extent to which the hydrolysis of the zirconyl sulphate had gone and also upon other conditions. Such basic precipitates are formed also on the addition of other salts of potassium. These crystalline precipitates are difficultly soluble in water and may be reprecipitated by the addition of  $K_2SO_4$ . They are fairly soluble in acids if they have been only slightly washed in water. If thoroughly washed they become practically insoluble in water or dilute acid. These basic double sulphates are decomposed by ammonia and are soluble in ammonium carbonate. By washing with water they are separated into a soluble substance richer in sulphuric acid and an insoluble one that is poorer. The solution of the former forms an abundant crystalline precipitate after standing a few days (760).

Rosenheim and Frank (609) prepared certain double salts with alkali sulphates which, they stated, might be regarded as alkali salts of a basic zirconyl sulphuric acid,  $Zr_2O_3(SO_4H)_2$ . These were obtained by precipitating cold concentrated solutions of  $Zr(SO_4)_2$  and an alkali sulphate with alcohol and washing with a little alcohol and ether. The product was quite homogeneous and consisted of very small, probably tabular crystals. They could not be recrystallized but suffered change on treatment with water. The following double salts were prepared:  $Zr_2O_3(SO_4K)_2 \cdot 8H_2O$ ;  $Zr_2O_3(SO_4Rb)_2 \cdot 15H_2O$ ;  $Zr_2O_3(SO_4Cs)_2 \cdot 11H_2O$ . No analogous salts were obtained with sodium and ammonium salts but amorphous basic products only. These salts presuppose the existence of a complex anion  $Zr_2O_3(SO_4)_2$ . Hauser and Herzfeld (300) have denied the accuracy of Ruer's work (621) and the existence of the complex anions  $ZrO(SO_4)_2$  and  $Zr_2O_3(SO_4)_2$ .

According to Chauvenet and Gueylard (134), evidence was obtained by cryoscopic and thermochemical methods of the existence of the following double compounds:  $2ZrOSO_4 \cdot SO_3 \cdot 3Na_2SO_4 \cdot 8H_2O$ ;  $3ZrOSO_4 \cdot SO_3 \cdot 2Na_2SO_4 \cdot 7H_2O$ ;  $ZrOSO_4 \cdot SO_3 \cdot (NH_4)_2SO_4 \cdot 3H_2O$ ; and  $ZrOSO_4 \cdot SO_3 \cdot 2(NH_4)_2SO_4 \cdot 3H_2O$ . Also the following:  $3ZrOSO_4 \cdot 2M_2SO_4$  and  $3ZrOSO_4 \cdot M_2SO_4$  where M represents K, Na or  $NH_4$ .

The complex and varying products obtained by mixing a solution of zirconyl sulphate with one of potassium sulphate have long been



a puzzle. In part, at least, mixtures of hydrolyzed substances are formed. Recently it has been shown (298) that if the mixed solutions are concentrated over sulphuric acid definite compounds crystallize. These show very well the influence of such a salt as potassium sulphate upon a progressing hydrolysis. When potassium sulphate is used micro-crystalline needles whose composition is  $K_4Zr_4(OH)_8(SO_4)_5 \cdot 8H_2O$  are obtained. In a solution strongly acid with sulphuric acid the first crystals formed are  $K_4Zr(SO_4)_4$ ; in weakly acid solutions the composition is that of potassium zirconium hydroxysulphate of varying composition. These products hydrolyze on being treated with water. If boiled with water, they become opalescent with colloidal zirconium hydroxide. Following the crystallizations in detail, the above-mentioned potassium zirconium hydroxysulphate,  $K_4Zr_4(OH)_8(SO_4)_5 \cdot 8H_2O$ , forms a crystalline crust of needles. A second crop of prismatic crystals is formed and these have the composition  $K_4Zr(SO_4)_4 \cdot 5H_2O$ . The first crystals hydrolyze to increase the free acid and bring about an equilibrium. The formation of the second then begins and decreases the amount of free acid. The reaction is thereupon reversed and the hydroxysulphate crystals form once more.

### Compounds with Selenious Acid

*Zirconium Selenite.* According to Berzelius (52) this is a white powder soluble in an excess of selenious acid. The basic zirconyl selenite,  $4ZrO_2 \cdot 3SeO_2 \cdot 18H_2O$ , was prepared by Nilson (517) by precipitating a solution of zirconyl chloride with sodium selenite. Kulka (417) claimed to have prepared the same salt by adding a solution of selenium dioxide in nitric acid to a solution of  $Zr(SO_4)_2$ . It was described as a jellylike precipitate soluble in hydrochloric acid. At  $100^\circ$  it lost fifteen molecules of water. Weibull (795) found this precipitate to have on drying the composition  $ZrO_2 \cdot SeO_2 \cdot 2H_2O$ .

The normal selenite  $Zr(SeO_3)_2$  is reported by Nilson (517) as being formed when the above basic salt,  $4ZrO_2 \cdot 3SeO_2 \cdot 18H_2O$ , is digested with selenious acid at  $60^\circ$ . The amorphous or colloidal precipitate is changed into microscopic crystals in the form of four-sided columns with sharply cut ends. This form is retained when they are heated to a temperature at which the selenium dioxide is driven off. They are difficultly soluble in hot hydrochloric acid, some of the selenium being volatilized as chloride. If a concentrated solution of

selenium dioxide is used the crystals are water-free and have the composition  $\text{Zr}(\text{SeO}_3)_2$ . With a more dilute solution one molecule of water of crystallization is present,  $\text{Zr}(\text{SeO}_3)_2 \cdot \text{H}_2\text{O}$ . This is probably a zirconyl salt following the analogy of the sulphite.

Selenious acid has been recommended by Smith and Jones (664) as a means of separating and determining zirconium.

### Compounds with Selenic Acid

*Zirconium Selenate.* This salt has been obtained by Weibull (795) as the tetrahydrate having the formula  $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ , thus corresponding to the normal sulphate and probably being hydrolyzed in the same way. It was prepared by dissolving zirconium hydroxide in selenic acid. It crystallized in transparent four and six-sided tables of the hexagonal system. Three molecules of water are lost at  $100^\circ$ , the fourth between  $120^\circ$  and  $130^\circ$ . The water-free salt is only slightly hygroscopic. It is soluble in water but only slightly soluble in concentrated acids or alcohol. Weibull also obtained basic products by hydrolyzing the normal salt with boiling water.

### Compounds with the Oxyacids of Tellurium

The compounds with these acids have been investigated only by Berzelius (59, 60). He reported the tellurite as a white, flocculent precipitate and the tellurate as a bulky, semi-transparent mass soluble in an excess of the zirconyl chloride solution from which it was prepared. The method of preparation was by the addition of a solution of sodium tellurite or, respectively, the tellurate to the solution of a zirconium salt such as the chloride.



## Chapter VI

### Compounds with Acids of the Nitrogen Group and Rare Inorganic Acids

#### Compounds with Nitric Acid

Berzelius (52) observed that a solution of zirconium hydroxide in nitric acid left on evaporation a yellow gummy mass which lost its acid radical on heating. If the heating was not carried beyond  $100^{\circ}$  the residue was completely soluble in water and the solution had the capacity of taking up still more hydroxide or could be neutralized with much alkali before a permanent precipitate was formed. Mandl (466) failed to prepare a neutral salt by the concentration of such a solution or a double salt by adding potassium nitrate. Müller (512) found no nitrate of constant composition but obtained always a mixture of the nitrate and the hydroxide formed during the hydrolysis, this hydroxide going into colloidal solution. Rosenheim and Frank (610) could obtain only zirconyl nitrate,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , which crystallized in well-defined forms. These, reduced to a fine powder, were dissolved by prolonged boiling in absolute alcohol, and from this solution ether precipitated a white powder. This was easily soluble in water and had the composition  $\text{Zr}_2\text{O}_3(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  or  $\text{ZrO}(\text{OH})_2 \cdot \text{ZrO}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Other observations reported by Hermann (320), Paykull (537), and Weibull (794) are manifestly erroneous from a failure to take into account the changes brought about by hydrolysis in the solutions. The zirconium nitrate of commerce is more or less basic zirconyl nitrate.

Chauvenet and Nicolle (135) have repeated some of these earlier experiments. The concentration of a solution of zirconium hydroxide in nitric acid over caustic potash did not yield the normal nitrate, nor did the evaporation of a syrupy solution at a low temperature in a current of carbon dioxide charged with oxides of nitrogen. The latter yielded only zirconyl nitrate. They concluded that the existence of the normal nitrate was doubtful. Certainly, if formed, it is most easily and rapidly hydrolyzed. They found that the methods hitherto used yielded only the zirconyl nitrate which crystallizes with two molecules of water. This remains unaltered in the air and does

not fume if entirely freed from adhering nitric acid. Efforts at dehydration even at the lowest possible temperature and in a current of carbon dioxide saturated with oxides of nitrogen failed, as some nitric acid always accompanied the water driven off.

The possible existence of other hydrates was investigated (135) by preparing various mixtures of  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  with water and measuring the heat of fixation of  $n$  molecules of water to the dihydrate.

$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	— aq.	=	$\text{ZrO}(\text{NO}_3)_2$	diss.	+ 2.17 cal.
“	.3 $\text{H}_2\text{O}$	“ “	“	“	— 0.50 “
“	3.5 $\text{H}_2\text{O}$	“ “	“	“	— 1.92 “
“	4.17 $\text{H}_2\text{O}$	“ “	“	“	— 2.77 “
“	4.76 $\text{H}_2\text{O}$	“ “	“	“	— 3.95 “
“	6 $\text{H}_2\text{O}$	“ “	“	“	— 5.90 “

The curve constructed with these data gave only one angular point corresponding to  $\text{ZrO}(\text{NO}_3)_2 \cdot 3.5\text{H}_2\text{O}$ . This hydrate forms at  $0^\circ$ , is unstable at  $10^\circ$ , and effloresces rapidly at ordinary temperature, yielding the dihydrate. Anhydrous zirconyl nitrate, according to these investigators, does not exist.

The effect of dilution on zirconyl nitrate was also examined (136). The dihydrate is very soluble and hydrolyzes immediately. The extent of this hydrolysis was measured by conductivity determinations on a N/100 solution at  $29.5^\circ$ .

Some minutes after preparation	$\lambda$	505.19
“ hours	“	554.
“ days	“	600.

At this point, it was apparently constant, remaining stationary for some months. There slowly formed a precipitate having the composition  $\text{ZrO}(\text{NO}_3)_2 \cdot \text{ZrO}_2 \cdot (\text{H}_2\text{O})_n$ , which may also be written  $\text{ZrO}(\text{OH})_2 \cdot \text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}_{n-1}$ . Of course, a number of reactions are possible in the changes measured above. An effort was made to determine these by neutralizing the liberated acid with N/100 NaOH and following up the neutralization by measuring the resistance. Portions (5 c.c.) of the zirconyl nitrate N/100 solution were taken. The results were as follows:

$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	NaOH	W.
5	0	257
5	2	302
5	4	344
5	5	373
5	6	407
5	7	437
5	8	470
5	10	545
5	12	487
5	14	411



Examination of the curve constructed from these data indicated the presence of two angular points corresponding to the two reactions  $\text{ZrO}(\text{NO}_3)_2 + \text{NaOH} = \text{NaNO}_3 + \text{ZrONO}_3$  and  $\text{ZrO}(\text{NO}_3)_2 + 2\text{NaOH} = 2\text{NaNO}_3 + \text{ZrO}_2$ . From this the inference was drawn that the constitution of the zirconyl solution in dissociating was  $\text{Zr}(\text{OH})_3\text{NO}_3 \cdot \text{HNO}_3$ . Cryoscopic measurements gave the molecular weight as 92.9 instead of 266.6, which meant that the number of independent particles probably numbered three. This is a helpful clue toward the solution of the problem, but of course leaves the identity of the independent particles unsettled. As to the progressive dehydration of the crystals by heat, it was found that dissociation began at  $120^\circ$  even in the presence of oxides of nitrogen. At this temperature a fairly constant weight can be obtained and the results indicated the presence of the basic nitrate  $\text{ZrO}_2 \cdot 3\text{ZrO}(\text{NO}_3)_2$ , as in the case of the sulphate. If dehydrated in air at  $110^\circ$  the substance  $\text{ZrO}_2 \cdot 2\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$  was left; at  $150^\circ$ ,  $2\text{ZrO}_2 \cdot \text{ZrO}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ; at  $215^\circ$ ,  $7\text{ZrO}_2 \cdot \text{ZrO}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ ; at  $250^\circ$ ,  $10\text{ZrO}_2 \cdot \text{ZrO}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ; and at  $300^\circ$  dissociation was complete with the formation of the end product  $\text{ZrO}_2$ .

Wagner (756) has examined what he called the temporary hydrolysis of zirconyl nitrate solutions with the aid of the ultramicroscope. Biltz (68) has dialyzed zirconyl nitrate solutions, finding the outside water free from nitric acid after five days and getting a colloidal solution of the hydroxide as a hydrosol which was clear in transmitted and cloudy in reflected light. The colloid was precipitated by electrolytes. The Tsigmondy gold number was found to be between 0.046 and 0.09 with a mean of 0.5.

Rosenheim and Frank could obtain no double nitrates with the alkali nitrates (610). When ammonia is allowed to act upon zirconyl nitrate ( $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ) a white, crystalline mass, scarcely hygroscopic and stable in the air, is obtained. The composition is given as  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{NH}_3$  (405).

### Compounds with the Acids of Phosphorus

On account of the scant and imperfect references in the literature it is impossible to give a systematic account of the compounds of zirconium and the zirconyl radical with the various acids of phosphorus. Investigations of such possible compounds along modern lines and based on a fuller knowledge of their probable behavior are needed.

Wunder and Jeanneret (828) have found that metallic zirconium is readily dissolved by a hot solution of phosphoric acid (Sp. Gr. 1.75). A clear, colorless solution results and whatever carbon was present is left undissolved. Further addition of water causes no precipitation. No effort to separate or determine the compound formed was reported.

Hautefeuille and Margottet (307) found that zirconium hydroxide was dissolved in phosphoric acid heated to a temperature short of dehydration and therefore probably in the form of pyrophosphoric acid. The amount dissolved was two parts in one hundred of the acid. On cooling two varieties of crystals separated from the fused mass. These were described as regular octahedra and cubic octahedra. They had high refractive power but showed no action on polarized light. They were not attacked by acids nor by potassium bisulphate but were easily decomposed by fusion with alkali carbonates, giving insoluble alkali zirconates which could be obtained free from the phosphoric acid. In this fusion the temperature was kept as low as possible and the exact equivalent of alkali carbonate used. This method of separation was used for the analysis, which gave the empirical formula  $\text{ZrO}_2 \cdot \text{P}_2\text{O}_5$ . This may be written  $\text{ZrP}_2\text{O}_7$  and the compound, therefore, is the pyrophosphate.

Knop (400) fused zirconia with sodium ammonium phosphate at a high temperature and for a considerable time. The cooled mass was leached with dilute hydrochloric acid. A white powder was left which was clearly crystalline under the microscope, the form being that of rectangular parallelepipeds. They resembled the crystals of sodium zirconium phosphate. The analyses are faulty but point to the same composition as above,  $\text{ZrP}_2\text{O}_7$ . It is by no means assured that these crystals did not contain sodium.

Weibull (794), making use of precipitation methods, obtained the following results: On addition of an aqueous solution of zirconyl chloride to an excess of disodium phosphate in solution a finely divided white precipitate was formed. This was insoluble in weak acids and in an excess of the disodium phosphate. It was slightly soluble in hydrochloric acid, more easily soluble in sulphuric acid. When dried it was insoluble in acids. By analysis its composition was shown to be  $\text{ZrP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ . A similar result was obtained by dropping a solution of zirconium sulphate into one of disodium pyrophosphate,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ , the analysis giving the composition as  $\text{ZrP}_2\text{O}_7 \cdot 1.5\text{H}_2\text{O}$ . Another experiment in which the solutions of zir-



conyl chloride and sodium phosphate were simply mixed gave a basic compound,  $5\text{ZrO}_2 \cdot 3\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ . Still another carried out in the same manner yielded a basic compound  $3\text{ZrO}_2 \cdot 2\text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , and the same result was obtained when phosphoric acid was used as the precipitant. Probably the zirconyl chloride solution used had the same previous history as to dilution, time, and temperature. A somewhat similar result but differing from the foregoing in the ratio of the components was obtained by the independent investigators, Hermann (319) and Paykull (537), on adding solutions of disodium phosphate to one of zirconyl chloride. They obtained precipitates whose composition was represented by the formula  $5\text{ZrO}_2 \cdot 4\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ . Such uniformity in results is confirmatory evidence that these are not accidental or indefinite mixtures but are regularly formed when the conditions are even approximately duplicated.

The experiments which have been detailed, therefore, show that when a solution of the zirconyl salt is added to an excess of a solution of any of the phosphates the result is the formation of the pyrophosphate. When, however, these conditions are not observed the result is the formation of basic zirconyl phosphates which vary according to the previous history of the solution of the zirconyl salt or, in other words, the extent to which hydrolysis has proceeded. With the exception of such basic compounds or mixtures as have been mentioned above the pyrophosphate is the only zirconium phosphate known. The marked tendency to form this instead of the other phosphates is noteworthy.

As to compounds with other acids of phosphorus, Hauser and Herzfeld (299) have reported that on the addition of sodium subphosphate,  $\text{Na}_4\text{P}_2\text{O}_6$ , in excess to a slightly warmed solution of zirconyl nitrate in dilute hydrochloric acid a fine, crystalline precipitate practically insoluble in dilute acid was formed. The composition of this zirconium subphosphate was given as  $\text{ZrP}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , and this on ignition gives  $\text{ZrP}_2\text{O}_7$ . Thorium forms a similar compound, which would have to be borne in mind when this reaction is used for analytical purposes.

These authors also stated that when hypophosphorous acid was added to a solution of zirconyl nitrate in water there was formed an amorphous precipitate which slowly dissolved in an excess of the precipitant. Any insoluble portion due to the presence of phosphates was filtered off. Electrolytic experiments showed the zirconium ions as complex, migrating with the negative stream. On the addition of

alcohol a precipitate consisting of fine crystals was formed. These had strong refractive powers and exhibited a double polarization. The composition was that of the hypophosphite  $\text{Zr}(\text{H}_2\text{PO}_2)_4$ . When freshly precipitated the crystals contained one molecule of water which was easily separated. They showed a peculiar light sensibility. By direct sunlight they were rapidly colored deep violet. In diffuse light this took place only after the expiration of a number of weeks. No dissociation could be detected in these colored crystals under the microscope.

*Double Phosphates with Alkali Metals.* Only those obtained with potassium and sodium phosphates are on record. With potassium the following compounds have been reported: Troost and Ouvrard (719) found that when zirconia or the phosphate or anhydrous zirconyl chloride were dissolved in fused potassium metaphosphate until no more was taken up and the cooled mass then leached with acidulated water to remove the excess of potassium metaphosphate there remained a double phosphate as a crystalline powder, apparently rhombohedral and belonging to the hexagonal system. These crystals acted strongly on polarized light and had a density of 3.18. They were not acted upon by acids nor aqua regia. The composition was  $\text{K}_2\text{O} \cdot 4\text{ZrO}_2 \cdot 3\text{P}_2\text{O}_5$ . When fused, potassium pyrophosphate was used as the solvent and treated in the same way a crystalline powder of hexagonal lamellæ was left and this also acted on polarized light. These were soluble in  $\text{H}_2\text{SO}_4$  but insoluble in  $\text{HCl}$  or  $\text{HNO}_3$ . The density was 3.08 and the composition  $\text{K}_2\text{O} \cdot \text{ZrO}_2 \cdot \text{P}_2\text{O}_5$ . On adding potassium chloride to the above fusion to make it more fusible, the same salt was obtained and, in addition, another insoluble double phosphate forming small tetrahedral crystals, which was not further examined. Fusion with the orthophosphate  $\text{K}_3\text{PO}_4$ , gave no definite results, but when  $\text{KCl}$  was added the same results were obtained as with the pyrophosphate. When these double phosphates were heated to a very high temperature all was volatilized except the zirconia, which was left in a crystalline form. The density was 5.73 at  $17^\circ$ .

*Sodium and Zirconium Phosphates.* Knop (400) prepared a double phosphate of sodium and zirconium by fusing zirconia with sodium ammonium phosphate and keeping it at a white heat for two hours. After leaching the cooled mass with dilute hydrochloric acid and removing an amorphous portion there was left a crystalline meal consisting of colorless, transparent crystals in the form of rectangular parallelopipeds which acted on polarized light. These crystals have



also been described by Wunder (825) as tetragonal combinations of prisms and basic pinacoids. Density determinations gave 3.12-3.14. They are insoluble in aqua regia. Analysis showed their composition to be  $\text{Na}_2\text{O} \cdot 4\text{ZrO}_2 \cdot 3\text{P}_2\text{O}_5$ , thus corresponding with the potassium compound. Troost and Ouvrard (719) using sodium metaphosphate as a flux with the addition of a small amount of sodium chloride, obtained rhombohedral crystals having a density of 3.10, whose composition was also  $\text{Na}_2\text{O} \cdot 4\text{ZrO}_2 \cdot 3\text{P}_2\text{O}_5$ . With sodium pyrophosphate as a flux small crystals whose form could not be well determined were obtained. The density was 2.88 and the composition corresponded to the formula  $6\text{Na}_2\text{O} \cdot 3\text{ZrO}_2 \cdot 4\text{P}_2\text{O}_5$ . These crystals acted slightly on polarized light, were optically bi-axial, and crystallized in hexagonal lamellæ. When a large amount of salt was used in the fusion prismatic crystals, which acted energetically upon polarized light with longitudinal extinction, were obtained. They were soluble in acids and had a density of 2.43. The analysis agreed with the formula  $4\text{Na}_2\text{O} \cdot \text{ZrO}_2 \cdot 2\text{P}_2\text{O}_5$ .

#### Compounds with Arsenic Acid

When disodium arsenate is added to a solution of  $\text{Zr}(\text{SO}_4)_2$  a white powder is precipitated in a hydrated condition. Dried at  $100^\circ$  there are two and a half molecules of water, Paykull (536); at  $110^\circ$ , one molecule Kulka (417). Analysis showed the composition to be  $2\text{ZrO}_2 \cdot \text{As}_2\text{O}_5 \cdot \text{H}_2\text{O}$  or  $2.5\text{H}_2\text{O}$ . When sodium arsenate was added to a dilute hydrochloric acid solution of  $\text{ZrOF}_2$  a voluminous white pre-one molecule, Kulka (417). Analysis showed the composition to be  $3\text{ZrO}_2 \cdot 2\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  (794). Berzelius (55) obtained an orange-yellow precipitate, which darkened on drying and was not decomposed by acids, by adding a solution of  $\text{NaSH}$ , saturated with  $\text{As}_2\text{S}_3$ , to a solution of a zirconium salt. The supernatant liquid retained a yellow color. He called the precipitate zirconium sulpharsenite. He also stated that tri- and disodium sulpharsenates gave with zirconium salts citron-yellow precipitates which became orange-yellow on drying and were not decomposed by acids.

#### Compounds with Antimonic Acids

When a cold, neutral solution of potassium pyroantimonate is added to a solution of  $\text{Zr}(\text{SO}_4)_2$  a curdy white precipitate is formed, insoluble in water but easily soluble in hydrochloric acid. The anal-

ysis of the air-dried sample showed the composition to be  $\text{ZrO}_2 \cdot \text{Sb}_2\text{O}_5 \cdot 7.5\text{H}_2\text{O}$ , or a hydrated pyroantimonate  $\text{ZrSb}_2\text{O}_7$  (417).

### Compounds with Chromic Acid

Weibull (794) reported that a precipitate was formed on adding a solution of chromic acid to one of zirconyl chloride, but no details were given as to the conditions observed in the experiment nor the composition of the product. Haber (276) stated that this precipitate was flocculent, orange-yellow in color, and difficultly soluble in dilute acid; also that the chromic acid could be gradually, though not completely, leached out with water. Venable and Giles (748) made a more detailed examination of this reaction and the resulting product. The use of an alkali chromate as the precipitant is inadvisable on account of the persistent retention of the acid originally in combination with the zirconyl, thus rendering the product impure. Zirconium hydroxide, prepared in the cold, was dissolved in a concentrated solution of chromic acid. A portion of this solution allowed to evaporate over a dehydrating agent in partial vacuum yielded no crystals but gave a small amount of a reddish-yellow precipitate which was probably a mixture of chromate and bichromate. When the solution was considerably diluted and boiled there was formed a yellow precipitate which was quite insoluble in water. This precipitate was granular or possibly very finely crystalline. The water of hydration was for the most part lost on heating at  $100^\circ$  and completely lost below  $200^\circ$ . Analyses of several preparations corresponded to the formula  $\text{Zr}_3\text{O}_5 \cdot \text{Cr}_2\text{O}_3$  on the dry basis, or, when the water present is taken into account,  $\text{ZrO}(\text{OH})_2 \cdot 2\text{ZrOCrO}_4 \cdot 2\text{H}_2\text{O}$ .

### Compounds with Tungstic Acid

Kulka (417) added to a solution of zirconyl nitrate in the cold a solution of ammonium metatungstate, obtaining a gelatinous precipitate. This precipitate, after boiling, was placed on a suction filter, washed with hot water, and then dried. The composition, deduced from the analysis, was  $5\text{ZrO}_2 \cdot 9\text{WO}_3 \cdot 33\text{H}_2\text{O}$ . By similar treatment of a precipitation made by means of sodium paratungstate a substance corresponding to the formula  $5\text{ZrO}_2 \cdot 7\text{WO}_3 \cdot 21\text{H}_2\text{O}$  was obtained. The composition of these precipitates was doubtless determined by the extent of the hydrolysis of the zirconyl salt used. These substances may be considered zirconium tungstic acids.



Kulka also prepared a potassium salt by dissolving  $\text{Zr}(\text{OH})_4$  in a boiling solution of potassium paratungstate. On concentration the excess of potassium paratungstate crystallized out. There formed a crop of lengthened elliptical crystals, microscopic in size, which had the composition  $\text{K}_2\text{O} \cdot \text{ZrO}_2 \cdot 2\text{WO}_3 \cdot 33\text{H}_2\text{O}$ . No further crops differing in crystal form were obtained by him.

Hallopeau (280) used a solution of potassium paratungstate ( $5\text{K}_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$ ) in which he dissolved  $\text{Zr}(\text{OH})_4$  by prolonged boiling. The solution was alkaline. It was filtered clear and crystals separated on standing. These were redissolved in boiling water and re-crystallized. The crystals were microscopic and feebly active optically. Analysis showed them to be potassium zircono-decitungstate,  $4\text{K}_2\text{O} \cdot \text{ZrO}_2 \cdot 10\text{WO}_3 \cdot 15\text{H}_2\text{O}$ . From the mother liquor separated a crop of very small prismatic crystals which acted with more energy upon polarized light with longitudinal extinction. These were potassium dizircono-decitungstate,  $4\text{K}_2\text{O} \cdot 2\text{ZrO}_2 \cdot 10\text{WO}_3 \cdot 20\text{H}_2\text{O}$ . Twelve molecules of this water were lost on heating at  $100^\circ$ . These zirconium compounds are less stable than the analogous ones of silicon.

Likewise, by dissolving  $\text{Zr}(\text{OH})_4$  in a solution of ammonium paratungstate and concentrating the solution over a dehydrating agent in partial vacuum to a syrupy consistency, there were obtained small, prismatic crystals which were strongly refractive and active to polarized light. They were easily dissolved in water and purified by re-crystallization. Their composition was that of ammonium-zircono-decitungstate,  $3(\text{NH}_4)_2\text{O} \cdot \text{ZrO}_2 \cdot 10\text{WO}_3 \cdot 14\text{H}_2\text{O}$ . Most metallic chlorides, nitrates, etc., gave insoluble precipitates with these compounds.

Berzelius (58) reported his experiments on the formation of zirconium sulpho-tungstate.

### Compounds with Molybic Acids

Since zirconium hydroxide is insoluble in ammonium molybdate solution, compounds can not be obtained by methods used for the tungstates. Kulka (417) prepared a molybdate by dropping a solution of ammonium molybdate into a cold solution of  $\text{Zr}(\text{SO}_4)_2$  until a permanent precipitate was formed. The precipitate is gelatinous and can be washed free from  $(\text{NH}_4)_2\text{SO}_4$ . It is insoluble in water but easily soluble in hot hydrochloric acid. The composition is  $\text{ZrO}_2 \cdot 2\text{MoO}_3 \cdot 21\text{H}_2\text{O}$ —zirconium molybdic acid.

Salts of a somewhat similar acid have been prepared by Pechard

(538). The ammonium salt was formed by adding, in small portions, ammonium fluozirconate to a solution of ammonium molybdate. The solution acquires a deeper and deeper yellow color. When this change ceases the addition of an excess of hydrochloric acid causes the formation of ammonium-zirconium molybdate. This forms yellow octahedral crystals whose composition is  $3(\text{NH}_4)_2\text{O} \cdot \text{ZrO}_2 \cdot 12\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ . The potassium salt is prepared similarly. In this case the crystals are brown and may be several centimeters long, and effloresce on standing. The composition is  $3\text{K}_2\text{O} \cdot \text{ZrO}_2 \cdot 12\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ . These compounds are analogous to those of titanium and tin.

### Compound with Vanadic Acid

A complex compound with vanadic acid has been prepared by Rogers and Smith (598). A solution of ammonium paratungstate was boiled for ten hours with an excess of zirconium hydroxide. Then ammonium phosphate was added and boiled two hours; and lastly, ammonium metavanadate, which had been reduced to the hydrate of the trioxide, was added and boiled two hours. Crystals separated from the concentrated solution in large black octahedra. They were very soluble in water. Nitric acid dropped on the crystals caused decomposition. The analysis showed the composition to be  $(\text{NH}_4)_2\text{O} = 5.35$ ;  $\text{ZrO}_2 = 0.63$ ;  $\text{V}_2\text{O}_3 = 14.28$ ;  $\text{P}_2\text{O}_5 = 2.49$ ;  $\text{WO}_3 = 62.29$ ;  $\text{H}_2\text{O} = 14.96$ . This substance was named by the authors ammonium-zircono-vanadico-phospho-tungstate. Similar complexes have been prepared for silicon, titanium, tin, and thorium.



## Chapter VII

### Compounds with Acids of the Silicon Group

#### Compounds with Titanic Acid

According to Berzelius, a precipitate of zirconium titanate is formed on mixing solutions of zirconium and titanium chlorides and adding to this a solution of potassium sulphate. Details are lacking and artificially prepared titanates have not been further investigated. A number of the zirconium minerals, however, carry appreciable quantities of titanium, also niobium and tantalum. In these it may be assumed that the oxides of the elements named form the acid constituents. Polymignite, for instance, contains 46.30 p.c. of  $\text{TiO}_2$  combined with 14.14 p.c.  $\text{ZrO}_2$ , 12.2 p.c.  $\text{Fe}_2\text{O}_3$ , 2.7 p.c.  $\text{Mn}_2\text{O}_3$ , 4.2 p.c.  $\text{CaO}$ , the remainder consisting of the oxides of the rare earths with traces of other oxides. Mengite is chiefly  $\text{TiO}_2$  combined with  $\text{ZrO}_2$  and  $\text{Fe}_2\text{O}_3$ .

#### Compounds with Silicic Acid

*Zirconium Silicate.* The natural silicate, known as the zircon or hyacinth, is the most abundant mode of occurrence of zirconium and also the most widely distributed. The crystal form is chiefly with the combination of faces [110], [111], often with a rhombohedral development and frequently thereby [311]. The faces [110] and [111] are usually well developed. An imperfect cleavage is shown along [110] and slightly also along [100] and [111]. They have a refractive action on light. They are to be classified as belonging to the tetragonal system of the bipyramidal class. The zircon is isomorphous with thorite ( $\text{ThSiO}_4$ ).

The crystals are usually opaque and of a brown-red color. Others are transparent and variously colored, though some are colorless. The opaque crystals also have a range of colors, but these are rarer than the brown-red. They vary in size from microscopic to several inches in length. The hyacinth is transparent and of a deep red color.

These and the transparent crystals are classed with the precious stones.

The zircon is found in igneous rock of various ages and also in the detritus from these. Though the zircon is very resistant to weathering agencies, a number of altered zircons are known. Among these may be mentioned alvite, anderbergite, auerbachite, beccarite, cyrtholit, oerstedtite, ostranite, and tachyaphaltite.

The following analyses of the zircons (unaltered) may be cited as showing the average composition:

Analyst	Locality	ZrO <sub>2</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
Klaproth	Norway	65.	33.	1.
Berzelius	Expailly	67.16	33.48	
Damour	North Carolina	65.30	33.21	
Chandler	Ceylon	66.92	33.40	0.67
Weatherell	Reading	63.50	34.07	2.02
Morehead	North Carolina	62.83	33.98	

A qualitative analysis of zircon from Green River, N. C., by Morehead (504) revealed the presence of Zr, Si, O, Fe, Na, K, Mg, Ca, Al, Pb, Sn, U, and Er. A more exhaustive analysis by Linnemann (449) gave nineteen elements as present, namely, Zr, Si, O, Na, K, Li, Mg, Ca, Al, Fe, Mn, Cu, Pb, Sn, Zn, U, Er, Bi, and Co. Pereira-Forjaz (539) reported from his electrographic study of Portuguese zircons the presence of Zr, Si, O, Ca, Al, Fe, Th, Ti, Mg, Sn, Bi, and Cu. Hannay (281) has reported traces of cerium and didymium. Thorium has been reported in a zircon from Schwalbenberg as present to the amount of 2.06 p.c. and yttrium as 3.47 p.c. (821). The iron content can be considerable, as much as 9 p.c. having been reported by König (406, 407). Some of these elements present doubtless may be regarded as impurities from infiltrations. The fairly regular presence of the five group analogues, Si, Ti, Th, Sn, and Pb, is, however, noteworthy. Zirconium also shows many analogies to the aluminum and iron which are always present. The absorption spectrum given by many zircons is ascribed to the uranium and rare earths present (36). As uranium is said to be always present, the radio-activity observed and also the accompanying lead may be assigned to this element. Zircons may be freed from iron and, in some cases, opaque zircons may be rendered transparent by heating them in an atmosphere of carbon tetrachloride, carbonyl chloride, or sulphur chloride.

Baddeleyite, the native zirconia ore from Brazil, also contains several of the analogous elements of the fourth group. In connection with it is found another natural zirconium silicate which may contain



as much as 75 p.c. of zirconia. This would appear to be a basic silicate. It differs from the ordinary zircon in its complete solubility in dilute hydrofluoric acid, which leaves the zircon unattacked. This is called zirkelite.

Zircon is not acted upon by dilute or concentrated acids. Hydrogen fluoride attacks it only at high temperatures. If mixed with carbon and heated to a high temperature it is acted upon by fluorine and chlorine. Its melting point has been lately determined (762) as 2550°. A mixture of  $\text{ZrO}_2$  and  $\text{SiO}_2$  in molecular proportions melts at the same temperature (762). Cussak (158) failed to melt it when using a Joly meldometer and drew the conclusion that the melting point was 1760° or higher. It is slowly taken up in a fusion with borax, also in microcosmic salt (340). The fusion with potassium or sodium hydroxide is also difficult and imperfect. The addition, however, of moderate amounts of sodium fluoride brings about a rapid and complete fusion.

The density of the zircon ranges from 4.0 to 4.7; the hardness from 7 to 8—therefore approaching that of the diamond. The formula is ordinarily written  $\text{ZrSiO}_4$ . Vegard (727, 728, 729, 730), from his study of the crystal lattice structure, reached the conclusion that the formula should be written  $\text{ZrO}_2 \cdot \text{SiO}_2$ , since the zirconium and silicon atoms were found to be similarly placed in regard to the oxygen atoms.

*Luminescence of Zircons.* It has long been known that zircons from certain localities, as Norway and Expailly, phosphoresce when heated to the temperature of low redness. Some of the zircons under this treatment become colorless and transparent; also, in most cases the density is permanently increased. A number of investigations have been made as to the cause and possible interrelation of these phenomena. Damour (161) has shown that there is slight and often inappreciable loss in weight on heating. Also, he has pointed out that the index of refraction is changed as well as the density, and that the increased density remains unchanged even when the heating is pushed to fusion, except in one or two of the cases examined. He suggested that it might be a matter of allotropism, the action of heat bringing about a change into the second allotropic modification. Fizeau (220) has shown that heat causes a lasting expansion of form. This would operate against an increase of density on heating. Experiments by Stevanovic (681), however, show that zircons having a density under 4.7 may have their density raised to that figure. The

range of density of the native zircons is from 4.0 to 4.7. Where the zircon has this maximum density already it is unchanged on heating.

The heating of a zircon then causes a slight loss of weight, which may be due to driving off some of the volatile constituents, a change of form, an increase in density, and a temporary phosphorescence. If the heating is for a brief period only, the phosphorescence may be re-induced by a repetition of the heating. After a few such re-heatings the zircon loses the power of phosphorescing on the application of heat. In some of the theories advanced to explain this luminescence it has been assumed to bear some relation to the color of the zircon, which may also be lost on heating. According to Henneberg (316) the luminescence appears at a temperature below that at which the color is lost or changed. The loss of weight ranges from practically zero to 0.45 p.c. of the weight and the change of density from 1.0 to 2.5 p.c. A brown-red color is lost at a temperature of about 300°. Spezia (671) drew the conclusion from his experiments that this loss was due to the reduction of the ferric compounds present and maintained that heating in a stream of oxygen restored the color. The experiments of Hermann (329) were more detailed and exhaustive and he agreed with Spezia that the color is largely due to iron in different stages of oxidation and, in the case of a green color, to an admixture of chromic oxide. Doelter (193) concluded from his investigation that Spezia was wrong in assuming that iron confers the color and thought it to be due to some unknown substance of a colloidal nature. With regard to density, he found the green zircon to have the lowest, and colorless zircon to have the highest. Green and yellow zircons, he believed, had a different coloring matter from the brown and red. Stevanovic (681) stated that the biaxial green zircon with a density of 4.3 changed on heating into the uniaxial, normal zircon with a density of 4.7. These phenomena attracted the attention of several earlier investigators and led to experiments on their part, but the varying accounts as to the properties and behavior of zircons may in part be explained by the somewhat wide variations of the minerals coming from different localities, the faulty methods of the investigators, and the neglect on their part to exclude the infiltrations of foreign matter which necessarily vitiate their results. Due precautions were taken by Doelter and other recent workers to remove, as far as possible, such matter as did not form a component part of the crystals. The cathode luminescence of the zircon was examined by Crookes (154) and Pochettino (558).



Further light has been thrown on these changes of color in zircons by a study of their radio-activity and the action of radium emanations upon them. The radio-activity of zircons is markedly greater than that of any other hard mineral occurring in igneous rock. Further, zircons contain hundreds of times more helium than the average rock with which they are associated and Strutt (690) has made use of this fact as a means of determining the geologic age of the surrounding rock. This radio-activity was in excess of the uranium or thorium contents and indicated the presence of an accumulation of radium. The uranium-lead ratio has been determined by Holmes (351), the percentage of uranium found being 0.0019 and of lead 0.000085. Zircons show also a greater radio-activity than any other mineral associated with monazite. Zircon crystals in plutonic rocks are opaque. Those in basalt and lavas are transparent and show signs of incipient fusion (690). The transparent crystals are thermoluminescent, giving out a phosphorescent glow and losing color when moderately heated (200°). The glow is not repeated if once heated until it disappears. Partial heatings bring out the glow until the property is lost. It can be restored, and also the color, by exposure for some weeks or months to the emanations from radium salts. Opaque crystals are not thermoluminescent nor made so by exposure to radium. Nor are they decolorized by moderate heating. If kept in melted basalt for twenty-four hours they become white, though not transparent, and then on exposure to radium emanations they become reddish-brown like the hyacinth and thermoluminescent. This treatment, however, does not make them transparent. It has been stated by Demarcay (174) that zircons lose their color when heated in a stream of carbon tetrachloride. Splinters of opaque zircons become transparent when heated in such an atmosphere or in one of carbonyl chloride, these reagents removing the iron, aluminum, and probably some other minor constituents.

To the radio-activity of zircons has been assigned (379) the production of the pleiochroitic halos observed in the enclosing biotite, iolite, etc. The color of zircons in monazite resembles that given to the glass containers by radium salts. This color penetrates the crystals. The theory of Doelter (194) that the colors of zircons may be due to some element in a colloidal state is in harmony with many of the known facts and receives support from the behavior toward radium emanations (490). The separation of the finely-divided, colloidal metal through the action of the rays is a possibility and it is

well known that the colorings given by a metal in this state may be greatly varied. It must be noted that not all zircons are affected by radium. Brauns (100) found that originally colorless specimens examined by him could not be colored. Grengg (260) believed that the finely-divided iron oxide surrounding zircon crystals in porphyries, which resembles the halos often surrounding zircon enclosed in biotite, was due to the decomposition of iron-bearing solutions circulating through pore spaces of the ground mass by emanations from zircon crystals.

As an accompaniment of radio-activity helium is found in zircons, euxenite (556), malacone (391), baddeleyite (9), and other zirconium minerals. Only 20 p.c. of the helium in malacone (whose radio-activity is very slight) could be attributed to the uranium present. The remaining 80 p.c. was due to something else, possibly radium, according to Kitchin and Winterson (391). On decomposing the mineral and treating it to separate the zirconia they found that the activity remained with the zirconia and insoluble material. Cumming (155) varied the treatment and found the soluble portion active. According to his treatment, this should have contained the radium. Kitchin and others have found that the helium in malacone was accompanied by argon, and Antropoff (9) detected argon in a zirconium mineral from Brazil. These anomalous observations have not been refuted nor any explanation offered. The same may be said of the observation by Ramsay and Usher (581) that a solution of zirconyl nitrate yielded carbon dioxide and carbon monoxide under the influence of radium emanations, as did solutions of the analogues Si, Ti, Th, and Pb.

*Artificial Zircons.* Deville and Caron (183) by passing at a high temperature silicon fluoride over zirconia or, reversing this, zirconium fluoride over quartz, obtained small octahedral crystals, transparent, brilliant, and having approximately the hardness and density of zircons. Hautefeuille and Margottet (306) by fusing a mixture of zirconia and silica in glacial phosphoric acid prepared a zirconium silicate. Hautefeuille and Perrey (309) on heating for a month two parts of zirconia and one part of silica with lithium dimolybdate to a temperature of 700°–1000° obtained ditetragonal, bipyramidal crystals having a density of 4.6. The crystal combination was [110], [111]. Chrustschoff (140) heated a mixture of the two hydroxides  $\text{Si}(\text{OH})_4$  and  $\text{Zr}(\text{OH})_4$  in a closed platinum crucible which was enclosed in a steel block for two hours at a red heat, thus securing a high pressure



in addition to the heat. The crystals were well-formed and up to 0.18 mm. in length. The density was 4.45.

*Natural Double Silicates.* Ordinary zircon is probably a mixture of zirconium silicate with small amounts of various double silicates. Certain other minerals are regarded as distinctively double silicates.

*Catapleiite* ( $\text{H}_2(\text{Na}_2.\text{Ca})\text{ZrSi}_3\text{O}_{11}$ ). Hardness 6; Sp. Gr. 2.8; monoclinic prismatic; cleavage perfect. On heating the crystals become uniaxial and go over into the hexagonal.

*Elpidite* ( $\text{Na}_2\text{Si}_2\text{O}_5.\text{Zr}(\text{Si}_2\text{O}_5)_2$ ). Sp. Gr. 2.5-2.6; rhombic prismatic.

*Eudialyte* ( $\text{Na}_{13}(\text{CaFe})_6(\text{SiZr})_{20}\text{O}_{52}\text{Cl}$ ). Groth regards the chlorine as due to some small admixture, as sodalite, and assigns the formula  $\text{Na}_2\text{O}.2(\text{CaFe})\text{O}.6(\text{SiZr})\text{O}_2$ .

*Lovenite* ( $\text{Ca.Fe.Mn.Na.ZrOF}.\text{(SiO}_3)_2$ ). Monoclinic; hardness 6; Sp. Gr. 3.5.

*Wöhlerite* ( $\text{Na}_7\text{Ca}_{10}\text{Fe}_3\text{Zr}_3\text{Si}_{10}\text{O}_{42}\text{F}_3$ ). This may also be mentioned.

*Artificial Silicates.* A. *Potassium zirconium silicate* ( $\text{K}_2\text{O.ZrO}_2.\text{SiO}_2$ ). This is formed by melting together at a bright red heat one part of zircon and four parts of potassium carbonate for fifteen minutes. If the heating is prolonged potassium silicate and crystalline zirconia are the products according to Ouvrard (531). This double silicate crystallizes in rhombic prisms (224). These are acted upon by hydrofluoric acid and ammonium fluoride (531).

B. ( $\text{K}_2\text{O.ZrO}_2.2\text{SiO}_2$ ). One part of pulverized zircon with two to four parts of caustic potash are heated in a silver crucible. The mass is leached with cold water, leaving the double silicate as a finely-divided powder (138, 46). The complete removal of the silica by prolonged heating with potassium carbonate was confirmed by Knop (400). When the fused mass was leached with water potassium silicate was dissolved out and potassium zirconate was left. Melliss (479) by a similar fusion obtained a microscopic, crystalline residue which on analysis proved to have the composition  $\text{K}_2\text{O.ZrO}_2.2\text{SiO}_2$ . The density was 2.79.

*Sodium Zirconium Silicate* ( $\text{Na}_2\text{O}.8\text{ZrO}_2.\text{SiO}_2.11\text{H}_2\text{O}$ ). This was prepared by Melliss (479) by the method used for the potassium compound, removing all soluble matter by leaching with water. The crystals were microscopically small, transparent, hexagonal prisms and had a density of 3.53. The water of hydration was lost at low red heat without indication of further decomposition. Sulphuric acid

decomposed the crystals. Another sodium zirconium silicate with the composition  $\text{Na}_2\text{O} \cdot \text{ZrO}_2 \cdot \text{SiO}_2$  was obtained by Gibbs (244) by fusing one part of zircon with four parts of sodium carbonate and leaching the residue by repeated boiling with a concentrated solution of sodium carbonate. The granular white powder which was left was washed with lukewarm water without decomposition. Bourgeois (94) added silica to powdered zircon and kept the mixture at red heat for twenty-four hours with a small amount of melted sodium carbonate. He found that a considerable excess of sodium carbonate decomposed the salt. He determined the crystalline form as rhombic prisms, 0.5 mm. broad and several mm. long. The facial combination was of [110] and [010] with angles of almost exactly  $60^\circ$  without end planes. The extinction was parallel and there was double refraction. The powder obtained by Gibbs (244) was decomposed by hot water and hydrochloric acid, and formed a jelly of silicic acid. The crystals obtained by Bourgeois were soluble in concentrated acids. There is doubt as to the formation of double silicates by these methods. According to Scheerer (638) and others, only the zirconates are formed in this way.

*Calcium Zirconium Silicate.* Berthier (46) made various trials at fusing zircon, quartz, and marble in carbon crucibles. The proportions were varied and some of the products were glassy, some enamel-like, and some dull and stonelike. The extent of fusion differed, as did also that of the homogeneity of the product. No definite compounds were reported. As has been stated, calcium is found in many natural zircons and these may contain small amounts of calcium zirconium silicate.

Berthier (46) also reported the results of his experiments in fusing zircon and litharge together. Two experiments were carried out on a small scale. The first yielded a translucent yellow mass, which on analysis gave Si, 0.097; Zr, 0.19; and PbO, 0.71. The second was semi-translucent and not homogeneous, showing partly olive and partly green coloration. The analysis gave Si, 0.15; Zr, 0.30; and PbO, 0.55. There is no proof of a definite lead zirconium silicate but some evidence that in some form the lead enters into the combination.



## Chapter VIII

### Zirconic Acid and the Zirconates

It would seem necessary to repeat here some facts already noted under the zirconium hydroxides. Normal zirconium hydroxide is readily dehydrated with the loss of one molecule of water:  $\text{Zr}(\text{OH})_4 = \text{ZrO}(\text{OH})_2 + \text{H}_2\text{O}$ . The change takes place in the presence of water on standing and is accelerated by heating. The resulting zirconyl hydroxide,  $\text{ZrO}(\text{OH})_2$ , is amphoteric, reacting with acids to form salts, as  $\text{ZrO}(\text{OH})_2 + 2\text{HCl} = \text{ZrOCl}_2 + 2\text{H}_2\text{O}$ . It reacts with bases to form salts of an acid,  $\text{H}_2\text{ZrO}_3$ , or zirconic acid. Analogous acids are  $\text{H}_2\text{SiO}_3$ ,  $\text{H}_2\text{TiO}_3$ , and  $\text{H}_2\text{SnO}_3$ . Whether a meta-zirconic acid may be formed also has not been definitely settled. Van Bemmelen (34) has adduced arguments in favor of the existence of such an acid. Complex compounds, which have been called poly-zirconates and which may correspond to the polysilicates, are known. The hydroxide,  $\text{ZrO}(\text{OH})_2$  or  $\text{ZrO}_2 \cdot \text{H}_2\text{O}$ , has been prepared by Ruer (619) and others by carefully drying the hydroxide (precipitated from either cold or hot solutions) at  $100^\circ$ , and by Van Bemmelen (34) by drying at  $140^\circ$ . The last molecule of water is practically removed at  $300^\circ$ , though it is partly lost at a somewhat lower temperature. The hydroxide, if dried below  $200^\circ$ , may be rehydrated, but if heated above that temperature rehydration is difficult and imperfect. If the temperature is raised rapidly to  $300^\circ$  while as much as one-third or more of this last molecule of water is still present, sudden dissociation takes place with the evolution of heat accompanied by light, and hence the loss of potential energy. The hydroxide  $\text{ZrO}(\text{OH})_2$  forms a hydrogel which may be obtained in the colloidal state. Observers have reported the radical  $\text{ZrO}$  as migrating with either the positive or negative stream.

**Zirconates.** Zirconic acid combines with strong bases to form compounds which are insoluble in water and are decomposed by acids. The slight solubility of zirconyl hydroxide in solutions of strong bases, as the caustic alkalies, practically limits the preparation of these compounds to fusion methods. The fact that when zirconium hydrox-

ide is precipitated by an alkaline hydroxide some of the latter is persistently retained has been looked upon as an indication that a compound has been formed. The alkali, however, can be removed by thorough washing and is doubtless merely adsorbed by the colloidal hydroxide. There is similar adsorption of acids, salts, etc. Some of the products of the fusion methods have been obtained in a crystalline form, others as powders only. The difficulty of deciding when a fusion reaction is complete leaves it uncertain at times as to whether unattacked zirconia is present, and no entirely reliable method for its separation has been used. The usual method is to wash free from the excess of base and then decompose and dissolve the zirconate with dilute acid. Discordant results, which seem to be due to the temperature or length of fusion, have been reported. It is noteworthy that experiments with the alkali bases show a wide variation and a tendency to form polyzirconates, while those with the alkaline earths are quite uniform, giving normal salts of zirconic acid.

*Sodium Zirconates.* When powdered zircon is heated for a considerable time at a high temperature with sodium carbonate and the resulting fused mass, after cooling, is thoroughly leached with water there is left, according to Knop (400), a crystalline sodium zirconate which is decomposed by hydrochloric acid. Ouvrard (531) stated that on using the same method he obtained only crystallized zirconia. If the temperature used by Ouvrard were high enough to volatilize the alkali this discrepancy might be explained, or the insolubility of the residue in water may have been considered sufficient proof that only zirconia was present. Earlier observations led to the belief that the zirconates were soluble and this error was repeated in books of reference.

Hjortdahl (342) attempted to determine the formation of sodium zirconates and their composition by heating together zirconia and sodium carbonate and measuring the carbon dioxide given off. Thus, when these two in approximately molecular proportions were kept at a dark red heat for nine hours all of the carbon dioxide was liberated and there was left a crystalline mass which was hygroscopic and on treatment with water yielded sodium hydroxide and an amorphous mass. From the carbon dioxide lost he concluded that a compound,  $\text{Na}_2\text{O} \cdot \text{ZrO}_2$ , had been formed, although he also heated sodium carbonate by itself and measured the carbon dioxide lost. The fusion was likewise repeated with powdered zircon and the same material



by Scheerer (638) and Hermann (319), each concluding that the material left after leaching with water was sodium zirconate.

Venable and Clarke (747) found that when zirconia was added to a clear melt of sodium carbonate it sank to the bottom and remained apparently unattacked for hours. In a number of experiments it was found that 90 p.c. and over of the zirconia was unaltered. After thorough leaching with water the mass was treated with dilute hydrochloric acid and the proportions of zirconia and soda in the solution determined. In two experiments the ratio was  $2\text{Na}_2\text{O} \cdot 3\text{ZrO}_2$ . In a third, where the heating was twice as long, the ratio was approximately  $3\text{Na}_2\text{O} \cdot 2\text{ZrO}_2$ . When sodium hydroxide was substituted for the carbonate a much larger amount of the zirconia entered into the reaction (40-60 p.c.). The ratio of  $\text{Na}_2\text{O}$  to  $\text{ZrO}_2$  in the hydrochloric acid solution was only from 6.7 to 7.8  $\text{Na}_2\text{O}$  to 93.3-92.2  $\text{ZrO}_2$ .

A so-called sodium perzirconate has been prepared by Pissarjewski (555) by mixing two grams of freshly prepared hydrated zirconium trioxide with 200 c.c. of hydrogen peroxide solution (2 p.c.) and 16 c.c. of sodium hydroxide solution (19.5 p.c.). On the addition of double the volume of alcohol an emulsion was first formed and then a flocculent precipitate. This was separated, dissolved in water at  $0^\circ$ , more hydrogen peroxide added with a few c.c. of sodium hydroxide, and then about three-fourths the volume of alcohol. The precipitate was washed with alcohol and ether and became a loose powder which was partially dried over dehydrating agents, washed again with alcohol and ether, and dried between filter paper and analyzed. This substance liberated hydrogen peroxide when treated with dilute sulphuric acid, and ozone and oxygen with concentrated sulphuric acid. The composition calculated from the analysis was  $\text{Na}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$ . It is difficult to classify this substance and the similarly prepared  $\text{K}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$ .

*Potassium Zirconates.* It is not practicable to prepare potassium zirconate by fusing zirconia in potassium carbonate because of its very slight solubility in that substance. Venable and Clarke (747) found that only 0.5 p.c. was dissolved after ten hours' heating. When potassium hydroxide was used from 45-75 p.c. was taken up, forming a compound which was insoluble in water but soluble in dilute acid. The composition varied when simply leached with water and the zirconate then taken up with dilute hydrochloric acid, indicating, perhaps, a partial decomposition of the zirconate. When dilute acetic acid was substituted for the leach water a substance was left which

had the approximate composition  $\text{K}_2\text{O} \cdot 3\text{ZrO}_2$ . This agreed with some of the results of Hjortdahl (342). It may be called a polyzirconate.

Potassium perzirconate ( $\text{K}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$ ) has been prepared by Pissarjewski (555) and shows the same properties as the sodium compound.

*Lithium Zirconate.* When lithium chloride is fused for some hours with zirconia or powdered zircon and the mass extracted with water, prismatic crystals with longitudinal extinction are left. These are soluble in acids. The composition is  $\text{Li}_2\text{O} \cdot \text{ZrO}_2$  or  $\text{Li}_2\text{ZrO}_3$  (531). The mass must be kept at a high temperature, as ordinary fusion shows little action (747). Fusion with lithium carbonate gives a strong evolution of carbon dioxide and zirconia crystallizes out of the melt.

*Lithium Perzirconate.* This substance was prepared (531) by fusing zirconia in lithium hydroxide and leaching the melt with dilute acetic acid. It had the composition  $\text{Li}_2\text{O} \cdot 2\text{ZrO}_2$  or  $\text{Li}_2\text{Zr}_2\text{O}_5$ .

*Magnesium Zirconate.* When a mixture of silica and zirconia is fused with magnesium chloride in a platinum crucible whose bottom is covered with ammonium chloride and the melt is raised quickly to a white heat and kept at that temperature for an hour (some of the magnesium chloride volatilizing and hence necessitating the use of an excess), a mixture of octahedral and prismatic crystals which can not be well separated is obtained. The prismatic crystals are reported as having the composition  $\text{MgO} \cdot \text{ZrO}_2$  (342). By heating a mixture of four parts of magnesium oxide and one part of zirconia and leaching the product with dilute acetic acid a crystalline salt with the same composition,  $\text{MgO} \cdot \text{ZrO}_2$  or  $\text{MgZrO}_3$  (747), is prepared.

*Calcium Zirconate.* Hjortdahl (343) reported an acid calcium zirconate which he prepared by heating powdered zircon or a mixture of silica and zirconia with an excess of calcium chloride for five or six hours at a bright red heat and leaching the product with dilute hydrochloric acid. It was described as a brilliant crystalline powder. The normal zirconate was prepared by Ouvrard (532) by heating zirconia in melted calcium chloride for 20-30 hours. The product was leached with water and a crystalline substance having the composition  $\text{CaO} \cdot \text{ZrO}_2$  was left. According to Venable and Clarke (747) this reaction takes place only after calcium oxide has been formed. They heated zirconia for many hours with calcium oxide and leached the product with dilute acetic acid. The crystals obtained (532) had a strong action upon polarized light and were apparently isomorphous



with calcium stannate and calcium titanate. The compound is the normal calcium zirconate,  $\text{CaZrO}_3$ .

*Strontium Zirconate.* Ouvrard (532) prepared this compound by fusing zirconia with strontium chloride. The reaction was brought about with greater difficulty than in the case of calcium zirconate. The crystals are similar to those of calcium zirconate. Venable and Clarke (747) fused zirconia with strontium oxide and leached the mass with dilute acetic acid. Both found the composition to be  $\text{SrO} \cdot \text{ZrO}_2$  or  $\text{SrZrO}_3$ .

*Barium Zirconate.* Ouvrard (532) obtained opaque crystals by fusing zirconia with barium chloride (difficult). Venable and Clarke (747) found that there was vigorous reaction when zirconia was fused with barium hydroxide. The product was leached with dilute acetic acid. It was crystalline. The composition was  $\text{BaO} \cdot \text{ZrO}_2$  or  $\text{BaZrO}_3$ .

## Chapter IX

### Organic Compounds

#### Compounds with Organic Acids

*Carbonic Acid.* It has been stated by early investigators that moist, gelatinous zirconyl hydroxide readily absorbs carbon dioxide from the air (43, 537). If the hydroxide is heated to  $100^{\circ}$ – $150^{\circ}$  in a stream of carbon dioxide for twenty-five to thirty hours the amount absorbed may exceed 16 p.c.; if suspended in water, as much as 7 p.c. may be taken up. This absorbed carbon dioxide is given off by the dried substance in a current of air, as much as 30 p.c. being lost in this way and the remainder on heating (743). When solutions of alkali carbonates are added to solutions of zirconyl salts, white flocculent precipitates soluble in an excess of the precipitant are formed. Boiling water poured on these precipitates causes the evolution of carbon dioxide with foaming. On being washed with cold water and dried over sulphuric acid the composition of such a precipitate in one analysis made was  $3\text{ZrO}_2 \cdot \text{Co}_2 \cdot 6\text{H}_2\text{O}$  (319). The solubility in an excess of alkali carbonate has been regarded as proof of the formation of double carbonates. It is possible that basic zirconyl carbonates are formed by some of these methods, but there is no evidence of the preparation of a normal zirconyl carbonate. Whatever compound is formed is very unstable, as is to be expected with so weak an acid.

*Formic Acid.* The addition of formic acid or an alkali formate to a solution of a zirconyl salt gives a precipitate which is soluble in an excess of the formate. An analysis of such a precipitate yielded  $\text{ZrO}_2$  76.35 and  $\text{HCO}_2\text{H}$  19.0 (466). When zirconium tetrachloride is dissolved in anhydrous formic acid all of the chlorine is liberated as hydrogen chloride and a crystalline crust, which is zirconium formate  $(\text{Zr}(\text{HCO}_2)_4)$ , is obtained (611).

*Acetic Acid.* Only insignificant amounts of zirconyl hydroxide are dissolved by either hot or cold acetic acid, even when glacial acetic acid is used (466, 743). The evaporation of such a solution leaves an amorphous powder which is soluble in water or alcohol (395, 722). This deposit has been described by Berzelius as being very hygro-



scopic, and also as being gummy, Mandl (446). It is manifest that the method is inapplicable for the preparation of a definite compound. When sodium acetate is added to a neutralized solution of zirconyl chloride and the whole heated the zirconium is completely precipitated as a voluminous, flocculent basic acetate. This is soluble in warmed glacial acetic acid and the evaporation of this solution leaves a brittle, gumlike mass (276). The re-solution of such a basic acetate in acetic acid does not yield a neutral acetate. The addition of acetic acid to a solution of a zirconyl salt causes an immediate precipitate which is redissolved by more acid (446).

*Zirconium Acetate* ( $\text{Zr}(\text{C}_2\text{H}_3\text{O}_2)_4$ ). Rosenheim and Hertzmann (611) prepared this salt by dissolving zirconium tetrachloride in boiling anhydrous acetic acid. After driving off the hydrochloric acid by heating the salt separated on cooling as microscopic prisms, easily soluble in water or alcohol but insoluble in ether. It is not very stable in air, losing acetic acid. The aqueous solution is quickly hydrolyzed.

The acetate is more quickly and completely hydrolyzed at a lower temperature than the salts of mineral acids. The hydrolysis was measured by the relative conductivity method and calculated in reciprocal ohms. The temperature at which the measurements were made was  $25^\circ$  (611).

#### Time Elapsed

5 Min.	25 Min.	45 Min.	18 Hrs.	23 Hrs.	41 Hrs.
$284.2 \times 10^{-6}$	$289. \times 10^{-6}$	$291. \times 10^{-6}$	$310. \times 10^{-6}$	$310. \times 10^{-6}$	$310. \times 10^{-6}$
Specific conductivity of the equivalent of acetic acid at $25^\circ = 289. \times 10^{-6}$ .					

The acetate lends itself especially to preparing the colloidal hydroxide for mordanting and similar purposes.

*Zirconyl Acetate* ( $\text{ZrO}(\text{C}_2\text{H}_3\text{O}_2)_2$ ). This is formed when the normal acetate is allowed to stand for a number of days over sulphuric acid. The normal zirconyl acetate is stable in dry air and is soluble in water or alcohol. In moist air it is hydrolyzed, giving insoluble basic products.

The chloracetic acids, butyric acid, propionic acid, etc., show a behavior analogous to that of acetic acid.

*Citric Acid*. Harris (286) reported the formation of a double citrate of zirconium and ammonium by the addition of ammonium citrate to a solution of zirconyl chloride. There was formed a white,

curdy precipitate which was washed and dried at 120°. It was very deliquescent. The analysis corresponded to the formula  $\text{Zr}_2 \cdot \text{C}_6\text{H}_5\text{O}_7 \cdot (\text{NH}_4)_3$ .

*Oxalic Acid.* Oxalic acid is the best solvent for zirconyl hydroxide among the organic acids, approaching the mineral acids in this respect (681). Solutions of zirconyl salts are precipitated by oxalic acid or ammonium oxalate, giving a gelatinous or flocculent precipitate which is nearly insoluble in water or dilute oxalic acid (202). Zirconyl sulphate presents some anomalies in this regard. This has been investigated by Ruer (617) and explained on the hypothesis of the formation of a zirconium-sulphuric acid, a supposition not accepted by later investigators. The precipitate formed with oxalic acid carries practically all of the zirconium. It was found by Venable and Baskerville (741) to be basic and to show a variable composition. It was nearly insoluble in dilute acids. Paykull (536) reported the preparation of an amorphous zirconyl oxalate,  $\text{ZrOC}_2\text{O}_4$ , and one with two molecules of water,  $\text{ZrOC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Rosenheim and Frank (610), on adding a solution of oxalic acid to one of a zirconyl salt, obtained a gelatinous precipitate which settled poorly and was filtered with difficulty. The addition of a solution of  $\text{NaC}_2\text{H}_3\text{O}_2$  caused the precipitate to settle readily, and it could be washed and filtered without difficulty. The air-dried precipitate was insoluble in cold water but was hydrolyzed by hot water. The composition was  $\text{ZrOC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ . When a boiling solution of oxalic acid was saturated with zirconyl hydroxide and the solution concentrated over  $\text{H}_2\text{SO}_4$  mixtures of large, clear, prismatic crystals of the oxalate and needlelike crystals of oxalic acid were obtained. These were separated mechanically and the oxalate analyzed. The formula given (610), namely,  $\text{ZrOH}(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$ , presents many difficulties. The compound is probably identical with that obtained by Venable and Baskerville (742) by analysis of the one formed when the precipitated oxalate is dissolved in a solution of oxalic acid to which some hydrochloric acid has been added. The analyses made by these authors gave the formula  $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 7$  (or 8)  $\text{H}_2\text{O}$ . The salt forms fine, prismatic crystals.

An ammonium zirconium oxalate  $(2(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{Zr}(\text{C}_2\text{O}_4)_2)$  has been reported by several investigators: Water-free (697), 4 molecules  $\text{H}_2\text{O}$  (536), 6 molecules  $\text{H}_2\text{O}$  (440). It can be prepared by dissolving zirconyl hydroxide in an excess of oxalic acid and nearly neutralizing with ammonia. Crystals form from the solution (742). These crys-



tals also form when ammonium oxalate is added to the oxalic acid solution of the hydroxide which should contain free acid (537). These crystals have been described as octahedra and as small monoclinic crystals. They dissolve in either cold or hot water without dissociation (507). A simpler method of preparation is to saturate a solution of an acid alkali oxalate with zirconium hydroxide. The formula has also been written  $\text{Zr}(\text{C}_2\text{O}_4\text{R}) \cdot 5\text{H}_2\text{O}$  where R represents the ammonium radical or an alkali metal (576).

*Tartaric Acid.* Zirconyl hydroxide dissolves in tartaric acid in a proportion of less than 1 : 1000. It is ten times more soluble in an ammoniacal solution of ammonium tartrate. The composition of the precipitate formed by adding a solution of tartaric acid to solutions of zirconyl salts varies under differing conditions of precipitation (794). The results obtained by Hornberger (356) do not accord with more recent investigations. Rosenheim and Frank (610) found that on adding tartaric acid to a solution of zirconyl chloride the precipitate settled well and was easily filtered. When air-dried it formed an amorphous powder, insoluble in water, easily soluble in mineral acids and caustic alkalis. It could be reprecipitated from the latter without alteration by the addition of acid. Various preparations under differing conditions yielded on analysis results corresponding to the formula  $\text{Zr}_3(\text{OH})_8 \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 6\text{H}_2\text{O}$  (611). The analyses reported fail to agree closely. By adding two atoms of hydrogen the formula may be rewritten  $2\text{ZrO}(\text{OH})_2 \cdot \text{ZrOC}_4\text{H}_4\text{O}_6 \cdot 7\text{H}_2\text{O}$ . This is probably only one of several basic tartrates which may be formed under more widely differing conditions. The solubility in caustic alkali indicates the existence of double tartrates. Rimbach and Schneider (593) observed that the addition of solutions of zirconyl salts to alkali tartrate solutions increased the action on polarized light. The above-mentioned basic tartrate, when dissolved in just the necessary amount of caustic alkali and the solution evaporated to a syrupy consistency, gave small, needlelike crystals which were very soluble in water. Analysis gave the composition as  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6 \cdot \text{ZrOC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ , which was reported (609) as  $\text{ZrO}(\text{C}_4\text{H}_4\text{O}_6\text{K})_2 \cdot 3\text{H}_2\text{O}$ . The same compound was prepared by mixing solutions so as to give the ratio two molecules of tartaric acid, one molecule of zirconyl nitrate, and four molecules of potassium hydroxide. Potassium nitrate first crystallized out and then potassium zirconium tartrate. The analogous sodium salt was not obtained. Solutions of zirconium tartrate in ammonium hydroxide gave products which were unstable, losing ammonia on standing. Rosen-

heim and Frank (610) looked upon the fact that many of these compounds with organic acids, when prepared under varying conditions, show a constant composition as evidence that they are definite compounds and not adsorption compounds as maintained by Müller (512).

*Benzoic Acid.* A compound of the normal zirconium benzoate with  $\text{ZrCl}_2$  has been prepared (611) by the action of an ethereal solution of benzoic acid at the boiling temperature upon zirconium tartrate, the boiling being continued so long as hydrogen chloride was liberated. The reaction proceeds according to the equation  $\text{ZrCl}_4 + 2\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H} = \text{ZrCl}_2(\text{C}_6\text{H}_5\cdot\text{CO}_2)_2 + 2\text{HCl}$ . The radical  $\text{ZrCl}_2$  functions apparently as the radical  $\text{ZrO}$ . Stronger monocarboxylic acids of the aliphatic series liberate all four of the chlorine atoms (see *Formic* and *Acetic Acids*).

By this same method a similar compound was obtained with ethyl benzoate. Two molecules of this ester and one of zirconium tetrachloride were heated with a reflux condenser. There was no evolution of hydrogen chloride. Crusts of brilliant crystals formed. The composition was found to be  $\text{ZrCl}_4(\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$ . These crystals were unstable in the air, liberating hydrochloric acid. Similar compounds were given with other esters, ketones, and aldehydes (611).

Basic zirconyl benzoates have been prepared by Venable and Blaylock (746) by adding a saturated aqueous solution of benzoic acid to a solution of zirconyl chloride. If the solution were cold the precipitate was finely granular, forming only after prolonged standing and settling slowly. It was evident that the precipitation was only partial. When the solutions were heated to boiling the precipitate was gelatinous, settling readily and easily washed and filtered. Both varieties of precipitate were dissolved by ammonium hydroxide. The precipitate was washed free of chlorine by hot water. The white precipitate continued to lose water on heating at  $100^\circ$  and darkened, hence the analyses were made on air-dried samples. The different preparations formed under varied conditions of dilution and washing were analyzed. The composition of these was, respectively:

No. 1,  $\text{ZrO}(\text{OH})_2 \cdot 2\text{ZrO}(\text{C}_6\text{H}_5\cdot\text{CO}_2)_2 \cdot 6\text{H}_2\text{O}$ ;

No. 2,  $\text{ZrO}(\text{OH})_2 \cdot 3\text{ZrO}(\text{C}_6\text{H}_5\cdot\text{CO}_2)_2 \cdot 16\text{H}_2\text{O}$ ;

No. 3,  $\text{ZrO}(\text{OH})_2 \cdot 6\text{ZrO}(\text{C}_6\text{H}_5\cdot\text{CO}_2)_2 \cdot 6\text{H}_2\text{O}$ .

Apparently no definite compound was formed but a series of basic zirconyl benzoates representing various degrees of hydrolysis. These may be mixtures or adsorption compounds of zirconyl benzoate and



the colloidal hydroxide. It is noticeable that the formula assigned to No. 1 corresponds to that reported by Rosenheim and Frank (610) to the tartrate prepared by them in a somewhat similar manner. This may be due to a coincidence of conditions under which the experiments were made, or may furnish an argument for the existence of this as a definite compound formed at a certain stage in the progress of the hydrolysis.

*Salicylic Acid.* The compound corresponding to the one with benzoic acid was prepared (611) by the same method. Zirconium tetrachloride was added to an anhydrous ethereal solution of salicylic acid and the whole kept at boiling temperature so long as hydrogen chloride escaped. Analysis gave the composition as  $\text{ZrCl}_2(\text{OC}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_3)_2$ . The hydrogen of the hydroxyl group combines with the chlorine to form the hydrogen chloride. It is obtained in the form of a white, crystalline crust. When the same reaction was tried with salicylaldehyde (the  $\text{ZrCl}_4$  being suspended in chloroform) a deep yellow, crystalline powder with the composition  $\text{ZrCl}_2(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO})_2$  was obtained. Similar results were obtained with other monohydroxy acids and aldehydes and also with ketones, but individual mention of these was not made (611). As already stated under the appropriate heading, this reaction gives with aliphatic acids compounds in which all of the chlorine is replaced by the organic radical.

A basic zirconyl salicylate was prepared by Venable and Giles (748). A saturated solution of salicylic acid was added to a solution of zirconyl chloride. A precipitate formed on standing or boiling. Three preparations were made in which the conditions varied more or less, especially as to dilution and amount of water used in washing. In other words, there was no effort at reproducing the exact conditions as to factors in hydrolysis. The analyses gave results showing the same product formed in the three experiments. The composition was  $2\text{ZrH}(\text{OH}_2\cdot 3\text{ZrO}(\text{C}_7\text{H}_6\text{O}_3)_2$ . This compound was less stable than the basic benzoic, decomposition, beginning at  $100^\circ$ , and the white precipitates were quite black at  $160^\circ$ . The samples were merely air-dried and contained varying percentages of water. This tendency to form one stable basic salicylate shows a decided difference from the benzoates.

The formation of a pyro-racemate (propanonate) has been reported (65); an acetyl-acetonate (69); and a valerianate (712).

*Hydrocyanic Acid and Thiocyanic Acid.* A solution of potassium

cyanide gives a precipitate with solutions of zirconyl salts according to Weibull (794). This has not been further investigated.

When barium cyanide is added in equivalent amount to a solution of zirconyl sulphate, barium sulphate is precipitated and zirconylcyanide remains dissolved. The solution is colorless and easily decomposed (794).

The thiocyanate has been prepared by Hornberger (356) by adding barium thiocyanate to a solution of zirconium sulphate. After removing the precipitated barium sulphate a colorless powder was obtained. This was unstable in the air, becoming yellow. Placed over sulphuric acid a yellow, amorphous mass, which turned brown on the water bath, was left. The analysis gave the composition as approximately  $\text{Zr}(\text{CNS})_2$ . The value of this work is doubtful as the author assumes zirconium to be bivalent. Rosenheim and Frank (610) saturated  $\text{HSCN}$  in alcoholic solution with  $\text{Zr}(\text{OH})_4$  and then precipitated with ether. The precipitate was white and easily soluble in water or alcohol. Double salts of the type  $\text{M}_2\text{H}_2\text{Zr}(\text{SCN})_6$  were obtained with pyridine and quinoline. These were crystalline, deliquescent, and unstable in air.

*Ferrocyanides.* The ferrocyanide was investigated by Weibull (794), Hornberger (356), and de Boisbaudran (88). The method of precipitation was from hot solutions of zirconium salts. Hornberger reported a compound,  $\text{Zr}_3\text{Fe}_2(\text{CN})_{12}$  or  $3\text{Zr}(\text{CN})_2 \cdot 2\text{Fe}(\text{CN})_3$ . The assumption of bivalence for zirconium would seem to make this work unreliable. De Boisbaudran (88) stated that ferrocyanide gave a yellow precipitate in solutions of zirconium salts even when very acid and dilute. Rose (600) reported a precipitate formed with potassium ferricyanide.

### Compounds of the Tetrahalides with Organic Radicals, etc.

The tetrahalides of zirconium form a number of addition compounds with the amines analogous to those formed with ammonia, also with organic bases. Substitution compounds are formed also with various organic radicals in which part or all of the halogen is substituted. The compounds formed with the tetrachloride have been the chief ones investigated.

In all such reactions in which these tetrahalides are concerned water must be absent. Since the tetrachloride reacts with alcohol, giving off ethyl chloride when heated and leaving zirconium hydroxide



(356, 337), this also can not be used as a medium. Attempts to form alcoholates, however, have failed (609). The tetrachloride is soluble in ethyl ether with indications of some reaction, since in concentrated solutions there are formed yellow crystals which are dissolved on further addition of ether and are rapidly decomposed independently of the presence of air. Similar crystals are formed by the tetraiodide and the analysis indicates the presence of  $\text{ZrI}_4 \cdot 4(\text{C}_2\text{H}_5)_2\text{O}$ . As alcohol was used in the reaction and the analyses were imperfect, the existence of this compound is in doubt. The crystals dissolved in water with violent reaction (674). Sometimes the reaction has been brought about by suspending the tetrachloride in a medium such as chloroform. Carbon tetrachloride might also be used, being inactive toward zirconium tetrachloride. Interaction between the vaporized substances has been seldom tried. The vapor of zirconium tetrachloride was found not to react with certain organo-metallic compounds, such as mercury ethyl or phenyl. It does react at temperatures over  $300^\circ$ , with methane or acetylene. These reactions have not been fully studied.

*Addition Compounds.* As double compounds with ammonia are formed by passing dried ammonia through an ethereal solution of zirconium tetrachloride, so similar compounds can be prepared with the amines and organic bases. Matthews (471) prepared a methylamine compound,  $\text{ZrCl}_4 \cdot 4\text{CH}_3 \cdot \text{NH}_2$ ; ethylamine,  $\text{ZrCl}_4 \cdot 4\text{C}_2\text{H}_5 \cdot \text{NH}_2$ ; propylamine,  $\text{ZrCl}_4 \cdot 4\text{C}_3\text{H}_7 \cdot \text{NH}_2$ ; pyridine,  $\text{ZrCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ . Pyridine hydrochloride,  $\text{ZrCl}_4 \cdot 2\text{C}_5\text{H}_5 \cdot \text{N} \cdot \text{HCl}$ , was prepared by Rosenheim and Frank (609) by saturating alcohol in the cold with hydrogen chloride, then saturating this with zirconium hydroxide, again saturating with hydrogen chloride, and adding to this a concentrated solution of pyridine hydrochloride. The micro-crystals obtained were fairly stable in the air after washing with alcohol and ether.

When anilin is added to a solution of zirconium tetrachloride in ether a gray precipitate, which seems to be stable when dry, is formed. This has the composition  $\text{ZrCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$  (471). In the same way was formed a compound with toluidine with similar composition,  $\text{ZrCl}_4 \cdot 4\text{C}_7\text{H}_7 \cdot \text{NH}_2$ . A gray-brown precipitate having the formula  $\text{ZrCl}_4 \cdot 2\text{C}_{10}\text{H}_7\text{NH}_2$  was given with  $\beta$ -naphthylamine and an analogous compound,  $\text{ZrCl}_4 \cdot 2\text{C}_9\text{H}_7\text{N}$ , was formed with chinolin (471). A chinolin hydrochloride has been prepared (609). This was microcrystalline and less stable than the corresponding pyridine hydrochloride. Its composition was  $\text{ZrCl}_4 \cdot 2\text{C}_9\text{H}_7 \cdot \text{N} \cdot \text{HCl}$ .

Chauvenet (125) prepared addition compounds with pyridine by dissolving zirconium tetrachloride in pyridine and evaporating the solution, water being excluded. Crystals showing the existence of two compounds were obtained. First, there was a compound,  $\text{ZrCl}_4 \cdot 4\text{C}_5\text{H}_5\text{N}$ , which decomposed at room temperature, more rapidly at  $50^\circ$ , or in vacuum at  $15^\circ$ . The loss by weight ceased when the composition  $\text{ZrCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  was reached. The latter decomposed at  $70^\circ$ – $80^\circ$ .

Zirconium tetrabromide forms analogous compounds: With ethylamine,  $\text{ZrBr}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ ; with pyridin,  $\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ ; with anilin,  $\text{ZrBr}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$  (471). There is also a pyridin bromhydrate,  $\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot \text{HBr}$ , which is much less stable than the tetrachloride compound (609).

Zirconium tetraiodide heated in vapor of ethylamine gives with strong evolution of heat a compound,  $\text{ZrI}_4 \cdot 6\text{C}_2\text{H}_5 \cdot \text{NH}_2$ . Other experiments in preparing addition compounds with the tetraiodide have been reported (674), but the methods adopted were open to criticism and analytical results unsatisfactory.

Zirconium thiocyanate also forms compounds with pyridin and chinolin analogous to those formed with the tetrahalides. The method of preparation is similar (610). A concentrated solution of thiocyanic acid in absolute alcohol was saturated with zirconium hydroxide and pyridin thiocyanate added. A yellowish, crystalline precipitate was formed. It was extremely unstable. The analyses indicated the composition as  $\text{Zr}(\text{SCN})_6 \cdot \text{HSCN} \cdot 2\text{C}_5\text{H}_5\text{N}$ . Similarly there was obtained with chinolin a compound with like properties to which the formula  $\text{Zr}(\text{SCN})_6 \cdot \text{HSCN} \cdot 2\text{C}_9\text{H}_7\text{N}_2$  was assigned.

Hinsberg (337) found that when  $\text{ZrCl}_4$  was dissolved in absolute alcohol and the solution boiled ethyl chloride was given off and zirconium hydroxide left. When zinc ethyl was added to powdered zirconium tetrachloride and heated to  $180^\circ$  in an atmosphere of carbon dioxide butane was given, due doubtless to the presence of some water. Rosenheim and Herzmann (611) concluded from their experiments that  $\text{ZrCl}_4$  formed a molecular compound with methyl ether. This they were unable to get in a pure state and subject to analysis. Molecular compounds were formed with esters by heating with ethereal solutions of  $\text{ZrCl}_4$ . For instance, when a water-free ethereal solution of two molecules of benzoic esters was mixed with an ethereal solution of one molecule of  $\text{ZrCl}_4$  and boiled with a reflux condenser a crust of white crystals formed. These were unstable in the air.



The analysis gave  $\text{ZrCl}_4(\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$ . Ketones, aldehydes, and esters of various monobasic acids gave the same reaction. In this reaction no evolution of hydrogen chloride was observed.

Peters (540) found that  $\text{ZrCl}_4$  did not react at  $200^\circ$  with  $\text{C}_2\text{H}_5\text{I}$  nor with  $\text{Hg}(\text{C}_2\text{H}_5)_2$ . If, however, slight moisture were present the reaction  $\text{ZrCl}_4 + 2\text{Hg}(\text{C}_6\text{H}_5)_2 + \text{H}_2\text{O} = \text{ZrOCl}_2\cdot 2\text{HgCl}\cdot\text{C}_6\text{H}_5 + 2\text{C}_6\text{H}_6$  took place. This substance was soluble in ether. When heated in a vacuum mercury phenyl chloride sublimed. Mercury ethyl and mercury o-tolyl gave no reaction.

Jefferson (373) has recorded precipitates as being formed by the action of a large number of organic substances upon an aqueous solution of zirconium nitrate. Among these were anilin, orthotoluidin, xylidin, dimethylanilin, di-ethylanilin, benzylamin, pyridin, piperidin, chinolin, etc. The nature of these precipitates is unknown. Hartwell (291) also reports a number of such precipitates.

Kolb (405) added antipyrin to an acid solution of zirconyl nitrate, evaporated on a water bath to a syrupy liquid, and then allowed this to solidify over a dehydrating agent. The formula assigned on analysis of the product was  $\text{Zr}(\text{NO}_3)_4\cdot 6\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$ .

## Chapter X

### Analytical Methods

#### Qualitative

No flame test is given by zirconium. It can of course be identified by the characteristic lines given in the spectrum, but this makes too great a demand upon the equipment and skill of the ordinary analyst. So delicate a test would doubtless reveal its presence as very widely distributed. Pereira-Forjaz (539) has made a spectrographic study of Portuguese minerals, finding zirconium in a number of them. Microchemical detection has been recommended by Behrens (37), who used the strongly refracting crystals of rubidium fluozirconate-rubidium fluoride,  $\text{RbF} \cdot \text{Rb}_2\text{ZrF}_6$ . Sodium-zirconium oxalate crystals and also those of the corresponding potassium compound have been used for this purpose (232, 304). Since one or both the double fluorides and double oxalates may be formed and the properties of the crystals differ, these microchemical tests would seem to be unreliable unless definite conditions of formation are maintained. The crystalline form of zirconyl chloride has also been proposed as a test. This form varies with conditions of crystallization, and extent of hydrolysis.

Blowpipe reactions for zirconia have been given by Florence (225). The behavior of zirconia in borax beads and in those of microcosmic salt has been described by Wunder (825). A number of investigators (291, 373, 466) have reported the precipitates given by organic bases. Brush (111) found that zirconium salts gave an orange-red with turmeric paper. According to Noyes (528), the color is more accurately described as pink. Titanium gives the same color. Kaserer (383) recommended as a color reaction that given by pyrogallol-aldehyde. This reagent gives with solutions of zirconium salts a yellow coloration and on boiling a dirty yellow precipitate and colorless solution. The same reaction is given with thorium salts.

A much used qualitative separation and detection is obtained by precipitation of the mixed chlorides with sodium hydroxide in mod-



erate excess. The hydroxides of Zr, Fe, Mn, Co, Ni, Ti, and U remain undissolved. These are washed and then dissolved in hydrochloric acid, the percentage of acid being brought up to 20-32. On shaking with ether zirconium chloride is left in the aqueous layer, though several shakings with fresh ether may be necessary (528).

Biltz and Mecklenburg (72) recommended a most delicate and useful qualitative test. The solution supposed to contain zirconium is strongly acidified with nitric or hydrochloric acid. A few drops of sodium phosphate are added and the solution warmed. A white, gelatinous precipitate is given when as little as 0.0005 per cent. of zirconia is present. No other element known to the authors gave such a precipitate in strongly acid solution. Iron, aluminum, the rare earths, beryllium, titanium, thorium, and silicon gave no reaction. When a mineral is to be examined it can be fused in a soda bead in the oxidizing flame, the bead dissolved in excess of hydrochloric acid, boiled, filtered, and a drop of the phosphate solution added. The test is not applicable if phosphoric acid is present in the mineral.

In analytical work with zirconium it should be borne in mind that all aqueous solutions of its salts have an acid reaction on account of the liberation of free acid by hydrolysis. Hence neutralization is temporary and even after carrying out the hydrolysis by boiling is only approximate.

### Quantitative Determination

Zirconium in combination with a volatile or organic acid is usually determined by direct ignition and weighing as  $\text{ZrO}_2$ . Errors may arise from two causes. In the first place, certain acid radicals are persistently retained, even after hours of heating over a blast lamp. In the case of chlorides, for instance, a fraction of a per cent of the chlorine is thus held. This small amount retained does not seriously impair the results in ordinary analyses, but becomes noteworthy where strict accuracy is required. The error here is in the direction of results that are too high. A second possible error arises from the extremely fine subdivision of the zirconia and the ease with which it is entrained and carried off by gas currents, such as those resulting from the burning of organic acids or the gases from the burner. This loss is not prevented by the presence of ammonium compounds as maintained by Bailey, but rather accentuated. If nitric acid is the one present the volatile radical can be driven off without loss under

the proper conditions. The error here is in the direction of results that are too low. Hence this may in part counterbalance the error mentioned above.

If the zirconium hydroxide has been precipitated by means of ammonium hydroxide and so is in the form of hydroxide, there is another source of loss which must be reckoned with. Whenever an aqueous solution of a zirconium salt stands or is heated hydrolysis takes place, so the hydroxide is always present and the necessary precautions for this condition must virtually always be applied. It has been found that unless the water has been driven off at least to 1 p.c. or less at a temperature below  $300^{\circ}$  then, on raising to that temperature or higher, the remaining molecules of water are lost with the evolution of much energy accompanied by incandescence and tiny explosions, thus causing the practical loss of substance. For careful work it has been found best to heat in an electric oven or air bath at a temperature between  $250^{\circ}$  and  $275^{\circ}$  for an hour or so. The water in the hydroxide is thus reduced below the danger limit. For organic radicals the temperature should be raised stepwise to  $250^{\circ}$  so as to insure the burning taking place at as low a temperature as practicable and a reasonably slow evolution of the gases. After the incomplete drying or burning the temperature is raised to  $300^{\circ}$ – $500^{\circ}$  and the last traces of water driven off at  $900^{\circ}$ – $1000^{\circ}$ . Analyses carried out in this way will give results higher usually by some tenths of a per cent than those obtained by direct and rapid ignition.

In many cases, as separations, etc., it is desirable that the zirconium be precipitated as hydroxide. Since this colloidal hydroxide retains persistently potassium or sodium hydroxide, this precipitation should always be done with ammonium hydroxide. The precipitation is practically complete and the solvent power of the precipitant when used in slight excess is negligible. The other hydroxides exert a slight solvent action. For the reason already given the ammonium salts formed should be thoroughly washed out before ignition. This is more or less difficult according to the condition of the gelatinous precipitate.

Various inorganic and organic substances have been recommended as precipitating the zirconium more or less completely from aqueous solutions, but on account of the hydrolysis going on in the solution, and hence the varying basicity of the salts contained in it, there is little certainty as to the nature of the product obtained on ignition unless the acid radical can be entirely volatilized, leaving only pure



zirconia. Thus oxalic acid has been used (741, 617, 621); lactic acid or salicylic acid (38, 746); thiosulphate (686, 325); sodium azide (157); acetic acid (276); chromate (276, 748); alkaline iodate (169, 102, 751); sulphurous acid (31).

The precipitation with phosphoric acid or an alkali phosphate has been frequently made use of in certain separations, determining the zirconium as phosphate, but the composition of this precipitate varies according to the extent of the hydrolysis. It has been chiefly used where the amount of zirconium present is quite small and the variations in composition negligible. The precipitate approximates in composition  $\text{ZrP}_2\text{O}_7$  (677). The use of the empirical factor  $\text{Zr} = 0.3828$  has also been suggested (216, 516). Precipitation by means of sodium subphosphate has also been suggested (412).

### Separation from Other Elements

Precipitation by means of ammonium hydroxide furnishes a method for the separation of zirconium from a number of other elements not precipitated by this reagent in dilute solutions. The colloidal nature of zirconium hydroxide and its strong adsorptive power must, however, be kept in mind. In some cases the thorough washing out of alkalies and other substances is difficult even with prolonged washing. Aluminum, manganese, the iron group, titanium, and uranium are precipitated along with the zirconium.

The separation from aluminum by means of an alkali iodate has been investigated (169, 102). The precipitation is quantitative in the presence of an excess of the reagent and also of nitric acid. Iodic acid may be used instead of the iodate (751). While this method will separate zirconium from a number of other elements, it can not be relied on for separation from thorium and titanium (412).

A complete and satisfactory separation from iron has been the object of much investigation, since this element is the most usual concomitant of zirconium and must be removed for a number of industrial uses. A complete list of methods used or recommended would have little practical bearing, as many of them are out of date and abandoned. For the remainder only the general principles involved can be indicated.

The weighed mixture of oxides may be heated in a current of hydrogen (595, 272, 273, 164, 165) or of phosgene (762) or the iron may be titrated (684). The mixed oxides may be treated with hydro-

gen chloride (312). The neutral solution may be treated with sulphur dioxide or alkali sulphites added (47, 319, 31), by adding ammonium sulphide in the presence of tartaric acid (573, 118, 356, 238, 401), by treatment with hydrogen peroxide or sodium dioxide (18, 238, 188, 191), by precipitation with nitroso-naphthol (401), by precipitation with thiosulphate (686, 326, 467). Electrolytic dissociation has also been investigated (144, 338). The separation of zirconium from iron in the presence of titanium and also when both titanium and thorium are present has been investigated (188, 189, 190). For separation from titanium a number of methods have been proposed (552, 326, 684, 172, 21, 16, 173, 188, 189, 190, 191, 108). Some of these make use of hydrogen peroxide as the precipitant. This precipitates both and the titanium may then be determined colorimetrically (188, 191, 6). Ammonium salicylate, sodium acetate, and acetone have also been used. Fractional precipitation by means of ammonium hydroxide at boiling temperature has been used for separation of titanium and columbium. The use of oxalic acid or alkaline oxalates has been investigated (246), but has been found unreliable if sulphuric acid is present (617).

Various methods have been suggested for separation from thorium (326, 246, 173, 563, 368, 190).

In its natural occurrence zirconium is always associated with silicon. The separation here is by the usual method of heating with hydrofluoric acid. There is a necessary precaution, however, namely, that an excess of sulphuric acid must always be present; otherwise some zirconia will be lost (784). Some of the sulphuric acid radical is also persistently retained and the ignition must be carefully and thoroughly carried out.

Cupferron, which is the convenient name for the organic compound nitroso-phenyl-hydroxylamine-ammonium, has been proposed as a precipitant for the separation and determination of zirconium. It was found that zirconium could be quantitatively precipitated by it in acid solutions (615). At first the amount of acid (sulphuric) which might be present could amount to as much as 5-7½ p.c. by volume (705), and this was later confirmed (218). The method was used successfully by Brown (106), and Lundell and Knowles (458) have recently shown that 40 p.c. of sulphuric acid may be present. Tartaric acid also does not interfere. Nitric acid decomposes the reagent. The iron must first be removed by precipitation with ammonium sulphide in the presence of tartaric acid. For separation



from aluminum the solution must be highly acid and the presence of tartaric acid is desirable. The presence of platinum or boric acid does not interfere, but that of phosphoric acid introduces a disturbing effect. The method is recommended as most exact. On ignition of the precipitate zirconia is obtained but the usual precautions to prevent loss must be observed. See also (40).

The method involving the use of phenylhydrazine has been recommended (4). This and the cupferron method of analysis, as well as the phosphate and the thiosulphate, have been comparatively investigated (467, 333).

An investigation of the various methods for determining zirconium has been made by Lundell and Knowles (458, 460). Objections to previous methods are detailed. The methods especially tested are those of Kelly and Meyers (387), Ferguson (216, 217), Johnson (375, 376), Travers (710), and Hillebrand (333, 334). A mode of procedure is recommended for the separation and determination of zirconium, especially in steels. The final precipitation is by cupferron, giving zirconia and titanic oxides on ignition. The titanium is determined colorimetrically.

## Chapter XI

### Technical Applications of Zirconium and Its Compounds

#### Precious Stone

The earliest use made of a compound of zirconium was that of the natural silicate as a precious stone. It was known under the names zircon, jargon, and hyacinth, and in early times was also supposed to have medicinal value. The use of the name hyacinth among the ancients was confusing as, besides the zircon, it sometimes meant the carbuncle and also a dark amethyst. The zircon, known by lapidaries commonly as the Ceylon zircon or jargon, was regarded as distinct from the hyacinth and was usually colored fire-red, yellow, yellowish-green, or gray. The hyacinth was distinguished as Oriental hyacinth. Its color was deep red with a touch of brown or sometimes of orange-red. Zircons show a great variety of colors from colorless to red, brown, yellow, green, gray, white, pink, and blue, besides intermediate tints. They may be translucent but ordinarily are opaque.

On account of its hardness (7.5) the zircon is cut with diamond powder or emery. It is cut in the rose, table, or brilliant form. The value depends chiefly upon the purity of the color. On account of its lustre and hardness it has been substituted for the diamond. Indeed, at one time it was supposed to be an inferior variety of diamond. It has been used in jewelling watches and as supports for the knife edges of fine balances. There is little demand for it at present in jewelry except in the case of fine crystals of pure color. At one time it was supposed to be peculiarly appropriate and was much used in mourning jewelry. The artificial preparation of zircons has been attempted (168, 182, 183).

#### Oxy-hydrogen Light

The brilliancy of the light given off by zirconia in the oxy-hydrogen flame was first observed by Hare (285) in 1820 in his effort to fuse it. After the development of the Drummond limelight it was



suggested that zirconia be used as a substitute for the lime, offering the advantages of slight absorbing power for carbon dioxide or water. In 1868 du Motay (507, 508) used it in one of the lamps lighting the Tuileries. Napoleon III was so pleased with the result that he ordered its installation in all of the lamps illuminating the court and gardens. The zirconia light attracted much attention on the part of inventors and others (66, 117, 167, 199, 287, 404, 451, 482, 535, 545, 657, 700, 740). On account of the purity of the light and the high emissive power of the zirconia it was recommended for scientific use (433), such as polariscopes, spectroscopes, etc., but this more especially refers to the next form.

### Gas Mantles

With the introduction of the Welsbach mantles interest in the Drummond light diminished. The first incandescent mantles made by Welsbach in 1880 consisted essentially of zirconia (810). Later this was largely substituted by the oxides of thorium and cerium, which have a higher emissive power. Zirconia is used in admixture with these and other rare earths (679).

### Incandescent Filaments

A number of attempts have been made to use metallic zirconium in the form of filaments in incandescent electric lamps. Its electrical conductivity and high fusing point should render it quite suitable for this purpose. Korolkow (411) has made an examination of the electrical resistance, emissive power, and expansion coefficient of zirconium filaments but such determinations are considerably affected by the presence of even small amounts of impurities. One difficulty which has to be met is the preparation of pure zirconium on a commercial scale and at a reasonable cost. Most of the experiments with zirconium filaments have been carried out with the more or less impure metal, sometimes associated with the carbide, which itself has been said to be unsuitable for the purpose. The properties of zirconium seem to favor its use as a substitute in part for tungsten should the difficulties in the way of its commercial production in a pure form be overcome, and its abundance and wide distribution would speedily make it replace the more costly metal. [See also Alloys.] A number of patents bearing on the manufacture of the filaments have been taken out (418-423). [See also Weber (769) and Wedding (771, 772).]

According to Meyer (486), investigators who have succeeded in producing malleable zirconium state that it has remarkable properties which fit it for use in the chemical laboratory as a substitute for platinum. So far nothing has been published on this subject.

### Reduction of Metals

A patent has been granted (385) for the use of ores containing zirconium in extracting gold, platinum, and other noble metals. The supposition is that zirconium in the metallic state is the active agent. Neither the chemistry nor the object of this patent is easy to unravel.

There is another patent (213) for the use of zirconium, its alloys with magnesium or aluminum, its carbide or phosphide, as a means of reducing other metals or forming alloys with them. The reaction is said to be exothermic and hence proceeds from its own heat after starting.

### Alloys

Various alloys of zirconium have been formed. The ferro and nickel alloys promise the greater usefulness. Bronzes have also been made. Cobalt, aluminum, and magnesium alloys have been placed on the market. Ferro-zirconium has been recommended in steel manufacture for removing oxygen and nitrogen. It has been offered commercially, containing 40-90 p.c. of zirconium. Small percentages of titanium have also been introduced.

The technically important alloys, chiefly those with metals of the iron group, are mentioned under *Patents*. In the earlier attempts to prepare the pure metal, certain alloys or zirconides, which led to confusion in the descriptions of the metal, were obtained. With aluminum there were made preparations, some crystalline, which contained varying proportions of aluminum (713, 714, 230, 489, 776). Such formulas as  $Zr_3Al_4$  and  $ZrAl_2$  have been assigned to these. Similar alloys were formed when magnesium was used instead of aluminum. There seems to be no tendency to alloy with metals of the alkali nor alkaline earth groups, nor with lead or copper. The alloys are often formed by thermo-electric or alumino-thermic processes.

It is claimed that these alloys are not subject to oxidation and that they are very resistant to chemical reagents. The alloys have a metallic lustre and some of them take a silvery, steel-like polish. They are readily malleable and may find a use as filaments for



incandescent lamps. Such filaments are claimed to have the power of selective radiations; in other words, emit more light than corresponds to the temperature to which they are heated by the electric current. This implies a considerably lower wattage per candle power than is now required by the average metal filament lamp (486). Analysis of one such alloy shows zirconium, 65 p.c.; iron, 26 p.c.; titanium, 0.12 p.c.; and al, 7.7 p.c. These alloys are produced by reduction with finely divided aluminum, together with the mixed oxides of iron, titanium, or whatever metal it is desired to introduce into the alloy. Or they may be produced by heating the mixed oxides in a graphite crucible in an electric furnace, using either zircon or zirkelite as a source of zirconium (486).

For use as a scavenger in casting steel a 20 p.c. ferro-zirconium is recommended in an amount equal to 1 p.c. of the weight of steel treated.

### Furnace Applications

Mixed with good conductors zirconia is said to improve furnace electrodes (759). On account of its low conductivity for both heat and electricity it can also serve as an insulating material. It is further used to replace thorium nitrate for coating the iridium bar and preventing the loss of iridium in the Heraeus furnace.

The oxide, zirconia, possesses physical and chemical properties which make it available for a variety of industrial uses. Among these properties are its high melting point and its low heat conductivity. On account of its low coefficient of expansion it withstands sudden changes of temperature. Its porosity is low, so that it is practically impervious to liquids. It is inactive toward most chemicals and is scarcely attacked by strong acids or alkaline fusion mixtures. It does not, however, resist the action of hydrofluoric acid and fluorides. Fused bisulphates also act upon it to some extent. It is, however, quite stable in the presence of most fluxes and slags.

As binding material, various organic substances, such as starch, organic acids, glycerine, tar, etc., have been recommended; also magnesia, phosphates, and borates. Since the native zirconia from Brazil is reasonably pure, it may be used direct with no other than mechanical treatment. Native zirconia begins to fuse at 1800°. For use in laboratories and chemical manufacture it is first purified. The chief impurities are iron, titanium, and silicon.

Working tests show that zirconia has much greater life duration

as a lining for furnaces than other refractories. In Germany experiments were carried out in a closed hearth steel furnace and it was found that the zirconia lining was good for eight months' use without renewal. This is several times longer than the usual life. Because of the low thermal conductivity the thickness of the lining could be reduced one-half, a two-inch lining being equal to four inches of chamotte. Furthermore, there was a saving of one-half in maintenance costs. In casting molds it shows a high resistance to steel, copper, brass, and bronzes.

It may be used as a protective coating for ordinary firebrick exposed to the action of acids or slags. In such cases, sodium silicate serves as a binding material; air-slaked lime may also be added. If it is desirable to increase the porosity and decrease the density organic substances or volatile salts may be added and burned out in the firing. It is of course detrimental to use a binder which may cause softening at comparatively low temperatures.

### Refractories

As a refractory, zirconia has also been used in making crucibles, muffles, pyrometer tubes, and for a variety of chemical wares. Combustion tubes made of it are said to be gas-tight up to 1000°. Crucibles and combustion tubes of zirconia have been used in the research laboratory of the Royal Berlin Porcelain Factory, as they possess great strength and also conduct electricity. They withstand high temperatures and sudden changes. Zirconia crucibles have been used for determining the melting points of pure iron, tungsten alloys, and platinum. Such ware can be plunged in water while red hot without injury. (For its use as a refractory see 13, 14, 278, 588, 589, 605, 624, 625, 626, 178, 290, 572.)

### Enamels

Zirconia is also used as an opacifying agent in enamels and a clouding agent in glass as a substitute for the costly stannic oxide and the poisonous compounds of antimony and arsenic. For this purpose it should be quite free from iron, and a number of processes have been worked out and some patented. General references follow (266, 267, 288, 336, 413, 430, 431, 432, 166, 592, 658, 675, 802, 762). The increasing demand for tin for other purposes and the limited supply may render this substitution necessary. According to some author-



ities, the zirconia has less covering power than stannic oxide. For cheaper ware native zirconia may be used, or ground zircon which has been treated with hydrochloric acid, then caustic soda, and finally leached with acidulated water. This would only partially remove the iron present.

### Glass

The use of zirconia as a clouding agent for glass has been mentioned above. A thorough comparison with stannic oxide in this application apparently has not been worked out. The addition of a small amount of zirconia to "vitresil" or silica glass is said to increase the tensile strength and resistance to bending or breaking, and to diminish the tendency to devitrification. The temperature at which the ware softens is practically unchanged. The appearance is not improved (3, 90, 494, 655, 702, 823).

### Textile Applications

Zirconium salts, as the hydrated sulphate or the acetate, have been used as a weighting filler for silk (429, 594, 678). The weight may be increased up to 50 p.c. Stannic salts are ordinarily employed for this purpose.

Various zirconium compounds are also used as mordants in dyeing (26, 642, 813) and in the preparation of lac dyes (642). Zircon white (799) is used as a pigment, having good covering powers and being unaffected by chemical agents (84). A patent has also been issued for the preparation of a zirconyl tannate (573).

It may also find a use as substitute for sodium tungstate or stannate in rendering cloth non-inflammable.

### Colloidal Applications

The colloidal properties of the hydroxide have been compared with those of other hydroxides and its use suggested in the purification of water (67, 68, 71).

### Medicinal

As "Kontrastin" it may be substituted for bismuthyl nitrate as a lining substance for the stomach, etc., in X-ray observations and radiographs. It has the advantage of being non-poisonous (803). This has been patented.

**Abrasive**

The carbide has been recommended as a polishing agent, abrasive, and for glass cutting (798, 801).

**Chlorinating Agent**

Willgerodt (816) has suggested the use of the tetrachloride as a chlorinating agent.



## Chapter XII

### Patents

1914. Arnold (11). U. S. Patent 1,121,890.

Utensils made of zirconia. The oxide is subjected to a high pressure. After withdrawing the pressure the substance is turned into a paste by means of a suitable fluid (water, alcohol, or the like), cast in molds, dried, and burned. The articles do not crack nor fissure. They may be glazed with titanium oxide, alumina, or silica. Similar articles made of thoria or the rare earths may be glazed with zirconia. The melting point of the glaze may be so arranged by mixing such oxides as to be a few hundred degrees over the highest temperature to which the article is to be exposed. The glaze is dried and burned on in a second heating.

1915. Askenasy (12). U. S. Patent 1,158,769. C. A. 10, 255.

Method of producing zirconia free from iron. This consists in heating the zirconium salt of a mineral acid (containing such impurities) under pressure to a temperature above the boiling point. Zirconium hydroxide separates out in an easily-filtered form and the impurities are left in the acid solution.

1909. Badische Anilin u. Sodafabrik (17). Ger. Patent 237,436. C. A. 6, 1507.

This patent refers to the preparation of zirconium nitride and its purification by treating with acid or oxidizing agents.

1920. Barton (28). U. S. Patent 1,342,084. C. A. 14, 2140.

Zirconium cyanonitride. Ore mixed with about 20 per cent of coke is heated in an electric furnace (with a nitrogen-bearing gas?). This yields a product containing Zr 82-84 per cent, C 3-5 per cent, and N 8-10 per cent. Cold 5 per cent  $H_2SO_4$  may be used to remove excess of iron. The product is golden yellow to bronze in color and has a specific gravity of 5.95-6.35.

1920. Barton (29). U. S. Patent 1,351,091. C. A. 14, 3301.

Zirconium oxide. This oxide may be produced from baddeleyite or zircon by melting with carbonaceous material, such as coke,

to form zirconium cyanonitride and the resulting product then heated with salt cake or niter cake.

1914. Böhm (85). U. S. Patent 1,099,110. C. A. 8, 2653.

This describes the fusion of zirconia in caustic alkali by means of an electric current. The zirconia is mixed with caustic alkali, which acts as an initial conductor and is later volatilized.

1914. Bosch and Mittasch (91). U. S. Patent 1,102,715. C. A. 8, 3353.

Purification of the nitride. Heat with air at  $700^{\circ}$  to burn out any carbon. Treat the residue with  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  or  $\text{FeCl}_3$  solution to decompose other impurities without decomposing the nitride.  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{MnO}_2$ , and a flux may also be used in oxidizing the impurities.

1919. British Thomson-Houston Co. (103). Brit. Patent 139,247. C. A. 14, 1960.

Alumino-thermic extraction of zirconium. Finely divided Al (80-200 mesh) mixed with 10 per cent fine flaky Al (60-200 mesh) is briquetted with zirkite,  $\text{Na}_2\text{SiO}_3$  serving as binder. The slag may be used as an abrasive.

1915. Brown and Cooper (107). U. S. Patent 1,151,160.

Production of ferro-zirconium. This alloy contains 40-90 p.c. of zirconium. It may also have 60-90 p.c. of zirconium along with an iron-group metal. It is malleable and ductile. The oxides of zirconium and iron (and titanium) are mixed with aluminum and the mixture ignited.

1916. Campbell and Carney (114). U. S. Patent 1,182,880. C. A. 10, 1918.

Separation of zirconium and thorium from the rare earths. The pyrophosphates of zirconium and thorium are insoluble in dilute acids. The pyrophosphates of the rare earths, except ceric salts, are soluble. Reduction by means of  $\text{H}_2\text{SO}_3$  renders the latter soluble also. Zirconium is then separated from thorium by the solubility of the oxalate in oxalic acid.

1917. Cooper (150). Can. Patent 179,121. C. A. 11, 3234.

Production of an alloy for cutting tools containing 8-15 p.c. of zirconium with 50 p.c. or more of nickel. It is free from iron or carbon and will not burn when cutting at high speed or grinding. The wear is small and the tool remains white.

1917. Cooper (151). Brit. Patent 112,259. C. A. 12, 1286.

Production of an alloy for cutting tools, electrical resistance,



etc. It contains 2-40 p.c. of zirconium, the remainder being nickel or cobalt. One or more metals of the chromium group may be added. The alloy may also contain up to 35 p.c. of molybdenum; up to 25 p.c. of zirconium, the remainder being nickel or cobalt; or up to 25 p.c. of tungsten and the remainder nickel and zirconium. These alloys are made by the thermo-aluminic method, the reactions taking place between mixtures of the oxides of nickel, zirconium, etc., or their ores and aluminum.

1918. Cooper (152). Can. Patent 185,436. C. A. 12, 1762.

Production of an alloy containing zirconium, nickel, aluminum, and silicon, which is especially adapted to cutting. The addition of silicon greatly increases the hardness. Zirconium modifies the physical and structural characteristics. A scleroscopic hardness of 65-75 is easily reached. Tungsten may be added.

1920. Cooper (153). U. S. Patent 1,350,359. C. A. 14, 3219.

Alloy for cutting tools. This may be used for high speed cutting tools and is composed of Ni 76.2 p.c., Zr 4.8 p.c., Al 2.0 p.c., Si 5.9 p.c., W 3.8 p.c., Fe 6.8 p.c., and C 0.29 p.c.

1920. Cyclops Steel Co. (159). Brit. Patent 151,981. C. A. 15, 667.

Corrosion-resisting steel alloy. This contains Fe of low carbon content, Si and Zr or other metal of the C group. The percentage of Si and Zr together is preferably about 2. Cr or Cr, Ni, and Mn may be added, the percentage of Cr being about 3-7 and of Ni about 5-20. In some cases about 0.3 p.c. Cu may be added.

1920. Dantsizen (166). U. S. Patent 1,343,040. C. A. 14, 2403.

Porcelain containing zirconium oxide.  $ZrO_2$  to the amount of about 15 p.c. is used in porcelain to improve its strength and electrical resistance at high temperatures. The porcelain may be formed of clay, 45; feldspar, 35; and zirconia, 15 parts.

1914. Dennis (175). U. S. Patent 1,115,513. C. A. 9, 27.

This describes a method for separating zirconium from the rare earths by electrolysis. The aqueous solution of the nitrates is subjected to the action of an electric current while maintaining the cathode surface substantially free from an adherent deposit. The current is at or above the lowest decomposition voltage of the first product desired. The deposition is fractional. The separate portions are removed as formed and the remainder is subjected again to the action of the current. The mercury

cathode is kept clean by forcing air through the mercury so as to agitate it and prevent any formation on the surface.

1913. Ehrich, Grätz, and Podszus (207). Ger. Patent 289,063. C. A. 10, 2438.

Production of filaments. Pure zirconium is ground to a fine powder. It is then worked into an emulsion with a liquid, such as  $C_6H_6$ ,  $CS_2$ , etc., and formed in filaments by pressure. These are heated by electricity in a non-oxidizing atmosphere close to the melting point and this temperature is maintained for a long time.

1918. Elektro-Osmose Gesellschaft (208). Brit. Patent 113,777. C. A. 12, 1415.

Use in enamels. Colloidal zirconium hydroxide as hydrosol is applied as a coating, dried, and fired at a temperature below the melting point. A small amount of water-glass may be added if desired.

1902. Escales (213). Ger. Patent 145,820. C. B. 1903, II, 1155.

A method of preparing metallic zirconium or its alloys. This involves the use of rare-earth metals or mixtures of their alloys with magnesium or aluminum. Carbides or phosphides of these metals may also be used, or mixtures of these, such as may be obtained by the electric melting of the phosphates, etc., mixed with carbon. The reduction process is endothermic.

1919. Eyer (215). U. S. Patent 1,314,861. C. A. 13, 2748.

A clouding composition for enamels. Zirconia is apt to produce spotted enamels and also they may become dull or tarnished on firing. Ordinary zirconium borate is free from these defects but has poor covering capacity. A highly basic zirconyl borate, as  $ZrO_2 \cdot 2B_2O_3 + 4ZrO_2$ , has much greater covering capacity and is free from the defects mentioned. The process consists in fusing together 7 parts of raw zirconia, about 3 parts of  $B_2O_3$ , about 2 parts of cryolite, and 5 parts of  $NaNO_3$ , allowing the mass to cool and powdering it.

1908. General Electric Co. (239). Brit. Patent 5,415. Soc. Chem. Ind. 28, 83.

Filaments for incandescent lamps. Filaments or other conductors are made from zirconium oxalate with just enough zirconium on heating to the necessary temperature without leaving any residual carbon. No binding material is necessary, since the oxalate forms a tenacious paste which can be squirted. The



oxalate may be prepared by precipitating a hot zirconium nitrate solution with ammonium oxalate. It resembles starch paste. The heating may also be applied to the production of alloys of zirconium.

1917. Glazebrook, Rosenhain and Rodd (247). Brit. Patent 112,973.

C. A. 12, 1111.

This covers a basic zirconyl sulphate and a basic zirconyl chloride. The sulphate is obtained by adding caustic alkali, such as  $\text{NH}_4\text{OH}$  or  $\text{NaOH}$ , to an acid solution of  $\text{Zr}(\text{SO}_4)_2$  until a permanent precipitate begins to form and then allowing the precipitation to proceed of itself. This basic sulphate may be converted into the oxide by ignition. Likewise a basic zirconyl chloride  $\text{Zr}_5\text{O}_8\text{Cl}_4 \cdot 22\text{H}_2\text{O}$  may be prepared, dissolved in water,  $\text{H}_2\text{SO}_4$  added and a sulphate  $5\text{ZrO}_2 \cdot 2\text{SO}_3 \cdot 14\text{H}_2\text{O}$  formed.

1920. Gordon (250). U. S. Patent 1,340,888. C. A. 14, 2242.

Preparation of  $\text{ZrO}_2$  from ore. Ore is fused with 3-4 times its weight of  $\text{Na}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{CaO}$  and 3-4 times its weight of  $\text{NaCl}$  or  $\text{CaCl}_2$ . Fusion at  $1000^\circ$ – $2000^\circ$  for 30-60 minutes, poured, cooled, pulverized.  $\text{SiO}_2$  separated with  $\text{H}_2\text{SO}_4$ , filtered, precipitated as  $\text{Zr}(\text{OH})_4$  and other bases by  $\text{NH}_4\text{OH}$  or other alkali.

1917. Grenagle (258). U. S. Patent 1,248,648. C. A. 12, 361.

Ferro-zirconium alloys. The object is to produce an alloy of zirconium, which, because of its selective radiation, will be useful for filaments in electric lamps, and in the manufacture of transformer elements. The process is one of co-reduction of compounds containing zirconium and iron, best in the presence of a titaniferous compound. This reduction may be brought about by aluminum. Thus  $3\text{ZrO}_2 + 3\text{Fe}_2\text{O}_3 + 5\text{Al}_2 = 3\text{ZrFe}_2 + 5\text{Al}_2\text{O}_3$ . This reaction may be carried out by heating the mixed oxides with aluminum in a graphite crucible with the electric current or oxy-acetylene flame.

1920. Grenagle (259). U. S. Patent 1,334,089. C. A. 14, 1266.

Zr-Nb-Ta alloy. Formed by heating the mixed oxides in an electric furnace. It contains Zr 6.8 p.c., Nb 53.5 p.c., Ta 39.7 p.c. It is not attacked by acids or alkaline solutions, does not oxidize or vaporize at white heat, and combines with C to form carbides which are hard and brittle. The alloy is malleable, ductile, and somewhat resembles Pt but is slightly yellowish.

1904. Guertler (269). Ger. Patent 182,200. C. B. 1907, I, 1518.

A method of changing difficultly crystallizable substances into crystalline form. The compounds or mixtures are dissolved in fused alkaline metaborates (e.g.,  $\text{NaBO}_2$ ) and this solvent driven off by heat, which is readily done at  $850^\circ$ – $950^\circ$  in a platinum crucible.  $\text{LiBO}_2$  is volatilized in 8 hours,  $\text{NaBO}_2$  in 4 hours, and  $\text{KBO}_2$  in 1 hour. Zircon can be crystallized in this way.

1909. Gustrow (271). Ger. Patent 189,364.

This refers to the use of zirconia as an opacifier in enamels.

1912. Hansen (283). U. S. Patent 1,026,392. C. A. 6, 1882.

Improvement in incandescent lamp filaments. This consists in forming threads made of refractory powder held together by a binder composed essentially of gelatinous zirconium oxalate, decomposable into a refractory oxide, and heating said threads in an inert environment to convert the oxalate into oxide and to consolidate and sinter the refractory metal.

1914. Hansen (284). U. S. Patent 1,084,629. C. A. 8, 871.

Improvements in zirconium lamp filaments. The process consists in mixing carbon with gelatinous zirconium oxalate, shaping the mixture into threads, then heating in an inert and rarefied atmosphere to produce coherent conductors of pure zirconium.

1912. Havas (310). Ger. Patent 262,009. C. A. 7, 3650.

This refers to the production of iron-free zirconia for enamels. A weak hydrochloric acid solution of a zirconium salt is heated in a closed vessel to temperatures above the boiling point (at ordinary pressure). Zirconium hydroxide separates out, is filtered, centrifuged, and washed. This is snow-white on ignition. Other acids besides hydrochloric may be used.

1913. Havas (311). Brit. Patent 9,153. C. A. 8, 3355.

This is apparently the same as preceding, only more detailed. The temperature to which the acid zirconyl chloride solution is heated is given as  $200^\circ$ .

1905. Heraeus (318). Ger. Patents 156,776 and 179,570.

These refer to the making of chemical apparatus out of zirconia.

1914. Herzfeld (330). Ger. Patent 290,878. Soc. Chem. Ind. 35, 634.

A process for obtaining pure  $\text{ZrO}_2$  from zirkite. The ore with excess of lime and carbon is heated short of complete reduction of the lime. The product is then treated with hydrochloric acid,



the silica removed, and the zirconyl chloride purified. Calcium carbide may be used in place of carbon.

1920. Hisamoto (341). U. S. Patent 1,345,441. C. A. 14, 2687.

Drawing filaments. Zr is surrounded by  $\text{ZrO}_2$ , enclosed in a tube of metal as Ni, and contents drawn to a filament. The tube and oxide are dissolved away with acid.

1920. Hutchins (364). U. S. Patent 1,362,316. C. A. 15, 583.

Refractory material. Such a material suitable for furnace linings, crucibles, or muffles is formed of a burnt mixture of zirconia and alumina.

1920. Hutchins (365). U. S. Patent 1,362,316. C. A. 15, 583.

Refractory material. A mixture of burnt zirconia and chromite is used as a refractory material for furnace construction and similar uses.

1914. Jost and Plöcker (380). Ger. Patent 285,981. C. A. 10, 1087.

Preparation of the silicide, oxide, and salts. Pulverized zircon is mixed with  $1\frac{1}{9}$  times its weight of coal and heated to whiteness. The silicide is formed and carbon dioxide escapes. The resulting mass is treated with dilute mineral acid and filtered away from the carbon. The salt is thus freed from silica and on ignition the oxide is obtained. It is useful for enamels.

1921. Kaiser (381). Can. Patent 207,290. C. A. 15, 667.

Alloys having high melting point and ductile properties are produced from such metals as Cr, W, V, Th, Zr, and Ru by adding one metal to another, which is used as a base, and adding a small amount of a second metal, which has a catalytic action, before sintering the mixture.

1887. Keepert (385). Ger. Patent 43,231. Ber. deutsch. chem. Ges. 21 c, 458.

Zirconium is described as having a great affinity for gold, platinum, etc. Zirconiferous ores are added to the material carrying the precious metals and the mixture is treated with a solvent. The undissolved material is separated and the precious metals precipitated. (This is seemingly meaningless.)

1913. Knöfler (397). Ger. Patent 285,934. C. A. 10, 1087.

This refers to the manufacture of refractory vessels. Pure zirconia mixed with some water is shaped by high pressure into suitable forms. Upon subsequent burning in furnaces at  $1400^{\circ}$ – $1600^{\circ}$  the articles acquire the requisite solidity and hardness with contraction. There is no sintering. The vessels may be heated

to 2000° and above for a long time without fusion. Thoria and the rare earths may be mixed with the zirconia.

1913. Knöfler (398). Ger. Patent 287,554. C. A. 10, 2134.

This is an addition to the preceding patent. Zirconia, or a mixture with thoria, without binding material is subjected to high pressure. After relieving the pressure the product is finely ground and then stirred with water or alcohol and poured into the forms, dried, and burned. The articles are readily removable from the forms. There are no cracks on drying or burning. The vessels are tight and not easily fractured.

1907. Kuzel (418). U. S. Patent 871,599. C. A. 1, 1930.

A method of converting elements into the colloidal state. This consists in first comminuting the zirconium and then treating the same under heat and agitation alternately with dilute solutions of an acid character, and then dilute solutions of a non-acid character, and between such treatments washing with pure inhibition liquid. The acid solutions may be organic from 0.5-20 p.c., or mineral acids or salts having an acid reaction. The basic may be 0.5-10 p.c. caustic alkali solutions, ammonia, or organic bases.

1907. Kuzel (419). Ger. Patent 204,496. C. A. 3, 881.

A process for making alloys of definite composition and objects therefrom. One constituent only need be in colloidal form (i.e., zirconium) and as many others as desired in the form of crystalloids, such as salts, oxides, hydroxides, acid salts, and halogen compounds. These latter are combined with the colloid by suitable means, such as precipitation of the colloid with an electrolyte until a plastic mass. This method is applicable in the manufacture of filaments.

1908. Kuzel (420). U. S. Patent 899,875. C. A. 3, 288.

A process for peptizing coagulated colloids of refractory elements free from carbon. This consists in treating such colloids with solutions of alkaline reaction and stopping such treatment before peptization begins. Zirconium is very easily peptized. The gel is peptized by treating with a small quantity of an alkaline solution—caustic or carbonate. Such peptized colloids have in a concentrated form a high agglomerative power for dry powders of any kind, as, for instance, metal powders, giving a plastic mass which can be formed in threads, etc. These



are dried and heated to a temperature exceeding the melting point. The colloid is converted into the metallic state. If powdered lead be added and the plastic mass molded projectiles of high density and great toughness are obtained.

1909. Kuzel (421). U. S. Patent 914,354. C. A. 3, 228.

Filaments for electric incandescent lamps. This consists of an alloy of antimony with such metals as zirconium. According to this method, filaments are made from plastic masses consisting of colloidal zirconium with or without the addition of the powdered metal and with or without the addition of the colloidal hydroxide. Antimony is incorporated into the plastic mass in a colloidal or finely-divided state, or, instead of antimony, sulphur or oxygen compounds of antimony may be used. This plastic mass is brought into the desired form, dried, and heated to a white heat. An alloy is thus obtained with antimony the presence of which gives a notable increase in the electrical resistance.

1910. Kuzel (422). U. S. Patent 969,064. C. A. 4, 2908.

A process for manufacturing articles with the use of colloids. A pasty colloid, preferably a peptized colloid, of lead or pulverulent lead to which finely-divided zirconium has been added is brought to the desired consistency and molded under high pressure. The articles are then dried and gradually raised to a temperature below the melting point of the ingredients in the absence of active gases.

1910. Kuzel (423). U. S. Patent 969,109. C. A. 4, 2909.

Solder for electrically connecting filaments of electrical incandescent lamps. The carbide of aluminum, to which may be added the carbide of zirconium to raise the melting temperature, is used.

1914. Kuzel and Wedekind (424). U. S. Patent 1,088,909. C. A. 8, 1408.

Preparation of pure zirconium. Mix  $ZrO_2$  and finely divided calcium. Enclose in a steel bomb and exhaust. Heat with a strong flame till reaction begins, then heat of reaction is sufficient. Cool gradually, finally in ice water. Treat contents with water, then dilute acid, to remove  $CaO$ . Grind, wash, and dry residue. To drive off gases completely, heat in vacuo to  $1000^\circ$ . Zirconium about 96 p.c. pure.

1912. Landau, Kreidl, Heller and Co. (432). Ger. Patent 294,202. C. A. 12, 413.

Use as a clouding agent for enamels. Alkali zirconium com-

pounds in hydrous form are used. The alkali content should lie between 2 and 7 p.c. The water content depends upon that of the alkali. The lower the alkali, the larger the amount of combined water. The water is only partially removed.

1913. Landau, Kreidl, Heller and Co. (429). Ger. Patent 258,638. C. B. 1913, I, 1629.

Use for weighting silk. This substitutes salts of zirconium for tin salts in weighting silk. It is carried out by the usual methods of practice with fixing baths.

1914. Landau, Kreidl, Heller and Co. (431). Ger. Patents 283,504, 281,571. C. B. 1915, I, 280.

These refer to the use of zirconium compounds in white enamels.

1909. Lesmüller (442). Ger. Patent 231,002. Chem. Ztg. Rep. 1911, 108.

Use for making sound castings. Zirconium in metallic form is added to the metal to be cast to insure a casting free from imperfections.

1910. Lesmüller (443). Ger. Patent 218,316. Chem. Ztg. Rep. 1910, 91.

Use as a clouding agent. Borax or boron trioxide melted with zirconia gives a colorless glass if enough of the borax is used. The solution of the zirconia is aided by the presence of silica. If cooled under steam or acid vapors, cloudings caused by the separation of double compounds with  $B_2O_3$  are given. By slow cooling the separation is avoided and amorphous, homogeneous masses are obtained. The enamel is stable towards acids and alkalies.

1914. Leuchs (444). Ger. Patent 285,344. C. A. 10, 375.

This refers to the purifying of zirconia. Add  $H_2SO_4$  to a solution of the chloride in the proportion  $7ZrO_2:4H_2SO_4$  and boil. Without applying pressure a readily filtered, crystalline, iron-free precipitate of basic zirconyl sulphate ( $ZrO_2 \cdot 3SO_3 \cdot 14H_2O$ ) is obtained. Precipitate with ammonia or caustic alkali, dry, and pulverize. The product is especially suitable for enamels.

1918. Loveman (454). U. S. Patent 1,261,948.

This is a process for purifying zirconia ores. Alumina and silica are removed by fusion with  $Na_2CO_3$  added in a ratio greater than 1 : 6 and leaching out the aluminate and silicate. The residue is then treated with dilute HCl, washed, and ignited.



1896. Müller-Jacobs (513). U. S. Patent 558,197. Ber. d. chem. Ges. 29, d, 448.

A method for manufacturing tannate of zirconium. This consists in dissolving a salt of zirconium in boiling water and slowly adding a saturated solution of tannic acid heated to boiling, washing and filtering the precipitate, and drying at a suitable temperature—not exceeding  $100^{\circ}$ . This may be used to decolorize solutions, to make lac dyes, to prevent or retard fermentation, and as an antiseptic.

1914. North (524). Ger. Patent 288,969. C. A. 10, 2461.

A method of recovering the valuable constituents in zirconium ores. The ore is added to molten, high-carbon iron to the complete saturation of the metal and the metallic solvent, then removed by dissolving in acids or burning off. In using ground ore ( $\text{ZrO}_2$  85.7 p.c.,  $\text{SiO}_2$  7.4 p.c.,  $\text{Fe}_2\text{O}_3$  4.1 p.c., and  $\text{TiO}_2$  0.6 p.c.) the residual mass has a very high melting point and approaches zirconium in properties.

1920. North and Loosli (525). Brit. Patent 155,299. C. A. 15, 1108.

Preparation of zirconium. Zirconium ore or oxide is reduced by mixing it with the theoretical amount of carbon and heating the mixture under increased pressure in an electric furnace. The current may pass through the charge itself or a conductive carbon core may be used.

1918. Norton Co. (527). Brit. Patents 113,958 and 113,959. C. A. 12, 1442.

Production of an abrasive. A crystalline product is obtained by fusing alumina and zirconia in an electric furnace, the proportion of zirconia ranging up to equi-molecular. Bauxite is calcined and mixed with zirconia. If desired, a small percentage of coal is added to reduce the iron oxide and silica. Powdered zircon may be used. The product, together with a binding material, may be formed into wheels, etc.

1920. Petinot (541). U. S. Patent 1,335,982. C. A. 14, 1519.

Alloy of zirconium and lead. This is formed by melting a mixture of  $\text{ZrO}_2$  and  $\text{CaO}$  in such proportions as to prepare  $\text{CaZrO}_3$ , adding sufficient carbon to reduce the  $\text{ZrO}_2$  to  $\text{Zr}$  and to form  $\text{CaC}_2$ , and then charging the resulting material into molten  $\text{Pb}$ .

1920. Petinot (542). U. S. Patent 1,335,983. C. A. 14, 1920.

Ferro-alloys containing zirconium carbide. These are formed by smelting a mixture of Zr ore, Fe, and C and rapidly cooling to prevent the formation of graphite. They contain zirconium carbide or a double carbide of Zr and Fe.

1919. Pugh (570). U. S. Patent 1,316,107. Chem. Met. Eng. 21, 742.

A process for preparing basic zirconyl sulphate. Sulphuric acid is added to an acid solution of zirconyl chloride in the proportion  $3\text{H}_2\text{SO}_4 : 5\text{ZrO}_2$  and heated. The product is  $5\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 13\text{H}_2\text{O}$ .

1920. Rare Metals Reduction Co. (582). Brit. Patent 138,348. C. A. 14, 1643.

Alloys for lamp filaments, electrodes, etc. These non-corroding alloys include Zr and Fe — Zr 40-90 p.c. or as low as 8.43 p.c. Ti, Al, Nb, Ta may be added and Fe replaced by Ni, Co, or Mn. The alloys are made by reduction of the metals, preferably in the presence of a titanium compound. All may be used in the reduction.

1915. Rietz (591). Brit. Patent 4,457. Soc. Chem. Ind. 35, 532.

Fireproofing and weighting silk by a uniform impregnation with the hydrogel of zirconium hydroxide. The material is steeped in a solution of a zirconium salt, e.g., zirconium acetate (obtained by evaporating a solution of zirconium nitrate and acetic acid). A neutral salt is added (as  $\text{MgSO}_4$ ), the product drained and heated for 45 minutes at  $60^\circ$ – $70^\circ$ . For fireproofing, the impregnated material is treated with dilute phosphoric acid, or precipitated zirconium phosphate is dissolved in a concentrated solution of oxalic acid and the material impregnated, with or without subsequent treatment with a neutral salt, and heated at  $70^\circ$ .

1921. Rietz (592). U. S. Patent 1,366,101. C. A. 15, 934.

Clouding glass, enamels, and glazes. Fluorides are used in conjunction with compounds of Zr. As example a frit consisted of  $\text{Na}_2\text{CO}_3$ , feldspar, quartz, native  $\text{ZrO}_2$ , and sodium silicofluoride. The fluorides are used in larger proportions than hitherto. The batches must contain a large proportion of  $\text{SiO}_2$ .

1919. Rosenhain and Rodd (606). U. S. Patent 1,307,881. C. A. 13, 2261.

Production of a basic zirconium sulphate. This is prepared



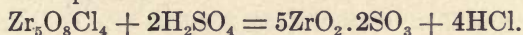
by adding an alkali, as  $\text{NH}_4\text{OH}$  to a solution containing zirconium sulphate and hydrochloric acid until so far neutralized that a permanent precipitate begins to form and then allowing the precipitation to proceed without further addition of alkali.

1919. Rosenhain and Rodd (607). U. S. Patent 1,307,882. C. A. 13, 2261.

Production of a basic zirconium chloride. This compound has the composition  $\text{Zr}_5\text{O}_8\text{Cl}_4 \cdot 22\text{H}_2\text{O}$  and is soluble in water. Dissolve wet  $\text{Zr}(\text{OH})_4$  in equal volumes of  $\text{HCl}$  and  $\text{H}_2\text{O}$  (D. 1.15); concentrate the solution until crystals form on cooling. These are mixtures of the above with  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ . On recrystallizing from  $\text{HCl}$  (D. 1.08) the basic chloride crystallizes alone.

1919. Rosenhain and Rodd (608). U. S. Patent 1,307,883. C. A. 13, 2261.

Production of a basic zirconium sulphate. This salt has the composition  $5\text{ZrO}_2 \cdot 2\text{SO}_3 \cdot 14\text{H}_2\text{O}$  and is sparingly soluble in water. It is formed from the basic chloride,  $\text{Zr}_5\text{O}_8\text{Cl}_4 \cdot 22\text{H}_2\text{O}$ , by dissolving in thirty times its weight of water and adding  $\text{H}_2\text{SO}_4$  according to the equation



1904. Ruff (622). Ger. Patent 286,054. C. A. 10, 956.

Preparation of zirconium carbide. The oxide is mixed with coal or placed in a carbonizing atmosphere and heated. For example, 1 k. crude or purified  $\text{ZrO}_2$  is mixed with 300 g. coal and heated in a graphite crucible. At about  $1900^\circ$  a copious evolution of gas sets in and continues on increase of temperature. It is raised to  $2100^\circ$ . There is direct production of a fine powder. The fineness is determined by the height of the final temperature.

1905. Sander (632). Ger. Patents 133,701, 137,568, and 137,569. C. B. 1905, I, 1290.

Zirconium incandescent electric lamps. The filaments are made of zirconium hydride and nitride or of zirconium carbide (90 parts) and rhodium (or the corresponding amount of oxide) (10 parts), which are worked into form by suitable methods. These filaments are very hard, not brittle, and have a metallic appearance. They conduct electricity as the metal does. The lamps are evacuated or filled with hydrogen. The normal efficiency in use is 2 watts per candle power. They burn 700-1000 hours and give only a slight deposit in the lamps.

1906. Sander (633). Ger. Patents 147,316 and 154,691.

These refer to the production of zirconium from the hydride and nitride.

1920. Sicard (656). U. S. Patent 1,335,991. C. A. 14, 1519.

Alloy of iron, zirconium, and titanium. This is formed by mixing baddeleyite, rutile, and scrap iron with carbon in sufficient quantity not only to reduce the oxides but to combine the metals to form a complex carbide which is smelted in an electric furnace. The alloy may contain Zr 35-40 p.c., Ti 4-5 p.c., C 4-8 p.c., and Fe 57-47 p.c., which may be used in forming zirconium steel.

1920. Sicard (657). U. S. Patent 1,335,992. C. A. 14, 1519.

Zirconium steel. This ferro-alloy is formed by adding the alloy of Fe, Zr, Ti, and C to molten steel. The Ti prevents oxidation of the Zr.

1913. Stern (678). Ger. Patent 261,142. C. B. 1913, II, 187.

Use for weighting silk. The fibers are impregnated with solutions of tungsten and molybdenum salts and then treated with a solution of a zirconium salt. Precipitate forms on the fiber. The baths may be reversed.

1914. Stern (679). Ger. Patent 276,423. Z. angewand. Chem. 27, 500.

This refers to the use of zirconia in gas mantles.

1919. Wade (755). Brit. Patent 153,113. C. A. 15, 930.

A new basic sulphate of zirconium of the composition  $5\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 13\text{H}_2\text{O}$ , free from Fe, Ti, and Si, is obtained by adding  $\text{H}_2\text{SO}_4$  in the requisite quantity to a solution of zirconyl chloride containing free acid, preferably HCl. The basic zirconyl sulphate is precipitated on heating.

1910. Weintraub (796). Brit. Patent 25,033. C. A. 6, 1406.

Preparation of pure zirconium. The metal may be prepared by the action of hydrogen upon zirconium halides at the temperature of the electric arc.

1919. Weintraub (797). U. S. Patent 1,306,568. C. A. 13, 2113.

Preparation of pure zirconium. Halogen compounds of zirconium, as the chloride, are reduced by the action of hydrogen mixed with the vapor of sodium or potassium in a reaction vessel heated externally by a gas burner and internally by an incandescent filament. The temperature is high enough to volatilize the NaCl formed but not to volatilize the metal—about  $1600^\circ$  abs. The gas stream may be omitted and the reduction take



place in a vacuum. The metal prepared in this way contains only 0.001 p.c. of impurities.

1910. Weiss (798). Ger. Patent 230,757. C. B. 1911, 320, or II, 524 (?).

This refers to the use of zirconia as an abrasive and polishing agent.

1910. Weiss (799). Ger. Patent 235,495. Chem. Ztg. Rep. 35, 320.

The preparation of white pigment and lacs. Starting with most of the compounds of zirconium (oxide, silicate, carbonate, phosphate, sulphite) a pure white pigment may be obtained on ignition. This is stable at high temperatures and most resistant to chemical action. It is not attacked by acid or alkali and not changed by hydrogen sulphide. It is not poisonous. It is worked up with the usual vehicles.

1910. Weiss (800). U. S. Patent 982,326. Chem. Ztg. Rep. 36, 320. Production of ferro-zirconium.

1911. Weiss (803). Ger. Patent 237,624. Chem. Ztg. Rep. 35, 1262.

This refers to the use of zirconia as an inert powder for medicinal purposes.

1885. Welsbach (810). Ger. Patent 39,162. Ber. d. chem. Ges. 20, Ref. 406.

The use of zirconia in gas mantles. This use is along with oxides of the rare earths, giving a white light. The making of the mantles is described.

1889. Welsbach (811). U. S. Patent 409,653. Chem. Ztg. 13 (2), 1192.

The preparation of zirconium nitrate. Zircon is pulverized, washed, digested with concentrated HCl to remove iron, mixed with twice its weight of  $\text{Na}_2\text{CO}_3$ , and heated to a white heat. The melt is leached with water and the insoluble residue treated with excess of  $\text{H}_2\text{SO}_4$ , which excess is later driven off. The zirconium sulphate is dissolved in water, precipitated by  $\text{NH}_4\text{OH}$ , and the zirconium hydroxide dissolved in nitric acid. This nitrate may be used in gas mantles.

1905. Wolfram Lampen Ges. (822). Ger. Patent 200,300. C. A. 2, 2909.

A means of overcoming the brittleness of tungsten filaments. Zirconium is added to tungsten and the filaments are formed with the addition of tin chloride-cellulose or glacial acetic collodion,

denitrated, sintered, decarbonized by heating in hydrogen, and heated to incandescence by electric current.

1907. Zerning (830). Brit. Patent 20,233. Soc. Chem. Ind. 27, 1197.

Lamp filaments. Heat zirconia with zinc dust in a hydrogen atmosphere. Then treat with acid to remove the zinc oxide and wash with water, alcohol, and ether, successively. The zirconium retains or combines with the hydrogen. Mix this product with 12-16 p.c. of a suitable binder, as nitro-cellulose in anyl acetate to which some castor oil has been added, and use to coat the inside of iron vessels in which lamp filaments are heated.



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